ACCSCIENCE PUBLISHING

Global Health Econ Sustain

ORIGINAL RESEARCH ARTICLE

Antimicrobial silver-loaded starch-based bioplastic grafted with poly(4-vinylpyridine) as a novel eco-friendly material

Supplementary file

This supplementary document shows a supplementary analysis of the effect of methanol washing and gamma-ray exposure (Table S1). This analysis describes the changes in grafting degree, Fourier transmittance infrared: Attenuated total reflection (FTIR-ATR) bands, and thermogravimetric analysis (TGA) thermograms.

(A) Effect of cleaning BP films before grafting

Preliminary grafting tests were performed using 50 vol% solutions of 4-vinylpyridine (4VP) in methanol at gamma-radiation doses of 10, 30, and 50 kGy. The results indicate that grafting 4VP onto unwashed films (BP*) yielded lower percentages compared to samples previously washed with methanol (BP) (Figure S1). These differences suggested that cleaning the

Table S1. Treatment conditions for bioplastics in this supplementary document

Sample	Pre-washed with methanol	Irradiated under air atmosphere (30 kGy)	Irradiated under argon and methanol medium (30 kGy)
BP*	No	No	No
BP	Yes	No	No
BPIA*	No	Yes	No
BPIA	Yes	Yes	No
BPIM*	No	No	Yes
BPIM	Yes	No	Yes

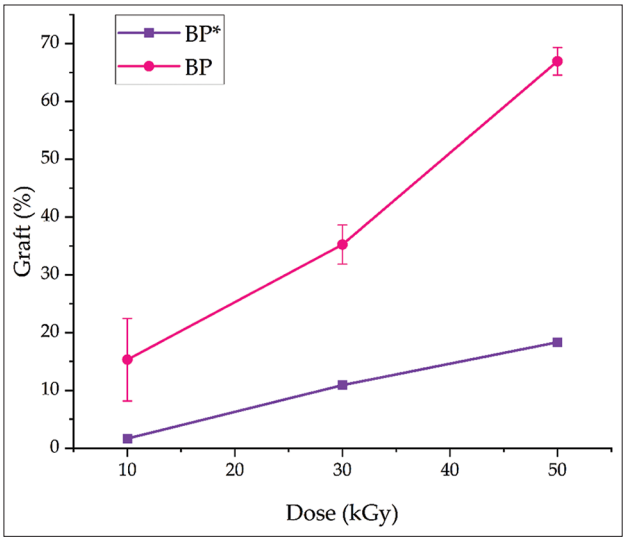

Figure S1. Preliminary experiments of BP films graft under argon atmosphere, utilizing a 50 vol% 4VP concentration in methanol as solvent, and irradiated at room temperature. The grafting of unwashed samples (*) was lower than that of pre-washed samples.

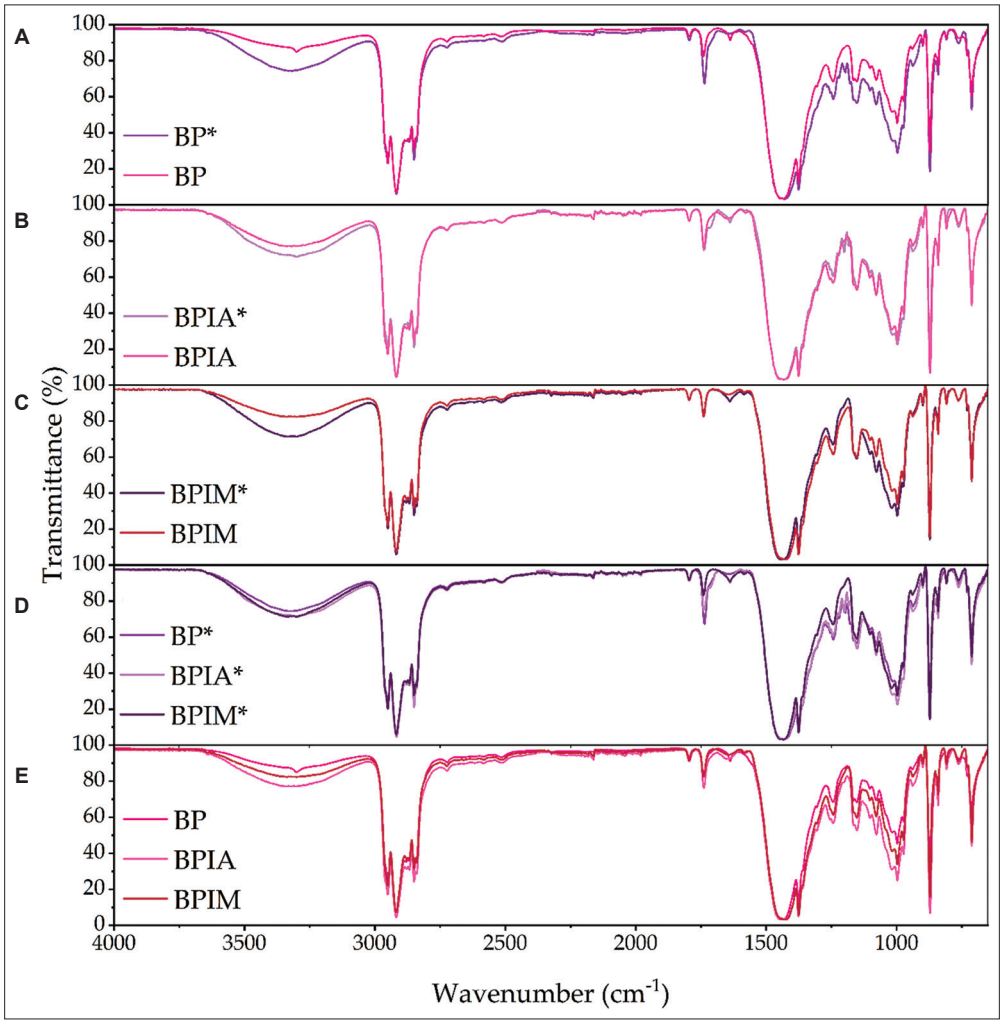

Figure S2. Fourier transmittance infrared-Attenuated total reflection spectra of BP films during the whole grafting process. It is observed how cleaning with methanol and exposure to irradiation changed the intensity on some bands. (A) Non-irradiated BP films but washed (BP) and unwashed (BP*) with methanol, respectively. The washed and unwashed films were irradiated under (B) an air atmosphere and (C) under an argon atmosphere with methanol as the medium. Finally, (D) unwashed films and (E) cleaned films are presented.

films before grafting is essential for achieving higher and reproducible results.

(B) Effects of cleaning and irradiation on BP films analyzed with FTIR-ATR

Unwashed and pre-washed BP films were irradiated at 30 kGy, both under an air atmosphere without any solvent and an argon atmosphere in a methanol medium. The results for all samples are displayed in the FTIR-ATR spectra (Figures S2 and S3), allowing us to compare the effects of methanol (used in pre-washing and the reaction) and gamma irradiation on pristine BP.

The non-irradiated but methanol-washed film (BP) showed a less intense OH stretching band in the region of 3500 – 3000 cm^{-1} compared to the unwashed (BP*)

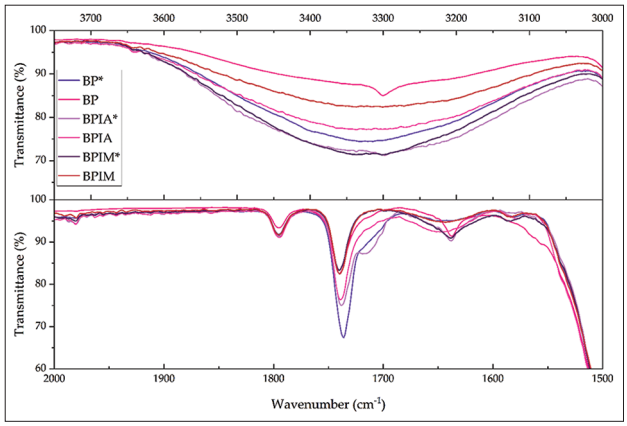

Figure S3. Overlapped Fourier transmittance infrared-attenuated total reflection spectra of different BP films with zooming in 3750 – 3000 cm^{-1} (top) and 2000 – 1500 cm^{-1} (bottom).

film (Figure S2A). A similar trend was observed for the unwashed film irradiated under an air atmosphere (BPIA*), which displayed a stronger OH stretching band than the pre-washed film (BPIA) (Figure S2B).

While infrared spectra of BPIM and BPIM* exhibited overlapped bands in the zone of 1500 – 750 cm^{-1} (Figure S2C), the non-irradiated samples BP and BP* showed bands with different intensities in the same region of 1500 – 750 cm^{-1} (Figure S2A). Therefore, pre-washing with methanol caused more changes in band intensities than irradiation in the fingerprint region.

Further analysis reveals that the clean film irradiated under air (BPIA) exhibited a stronger OH stretching band than non-irradiated BP, primarily due to the formation of hydroperoxide groups resulting from irradiation. In addition, BPIA displayed a stronger OH stretching band than BPIM because the methanol medium, purged of air, is less oxidizing, and methanol also dehydrated the film (Figure S2E). In contrast, the difference in intensity in this OH stretching band was barely observed in unwashed films (Figure S2D), indicating that pre-washing with methanol is the most important factor for the removal of methanol-soluble impurities, absorbed water, and plasticizer.

Finally, in the carbonyl region at 1750 cm^{-1}, a relevant change was detected among the BP* and BPIM films because, once again, methanol removed solvent-soluble impurities, absorbed water, and plasticizer before and during irradiation; for that reason, the pristine BP* has the stronger carbonyl band (Figure S3).

Based on these observations of the infrared bands, it can be inferred that methanol, when applied before, during, and after irradiation, helped remove solvent-soluble impurities, water, and plasticizer from samples. Furthermore, irradiation slightly increased the oxygen groups (hydroxy and carbonyl) in BP, which is consistent with the gamma-induced grafting method.

(C) TGA of BP films to study the effects of cleaning and irradiation

TGA was conducted on samples BP*, BPIA*, BPIA, BPIM*, and BPIM, revealing subtle differences in the corresponding thermograms (Figure S4).

The decomposition temperatures (TD) (Table S2) in the ranges of 200 – 399°C and 400 –549°C were found to be quite similar for all samples, indicating that the backbone of the BP (a stable composite) was not significantly affected by pre-washing with methanol or exposure to 30 kGy of gamma radiation in either air or purged methanol medium. However, significant variations were observed in the TD range of 25 – 199°C (Table S2), with the first TD being higher in BP* (around 140°C) and decreasing in the irradiated and mainly in the washed films. The first TD of pristine BP* film was higher than that of the others because methanol, used in the washing process, aided in the removal of soluble impurities, plasticizer, and absorbed (and/or occluded) water, resulting in minimal impact on the thermal properties of the first stage (Figure S5). Conversely, and for the same reason, the TD in the temperature range of 550 – 800°C occurred earlier for BP*, as volatile impurities, water, and plasticizer were not removed before heating. However, temperatures associated with a 10% weight loss and residue remained virtually unchanged (Table S3).

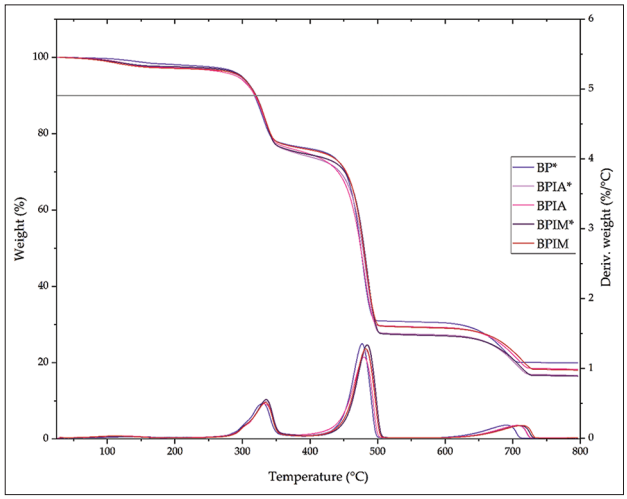

Figure S4. Overlapped thermogravimetric analysis thermograms show the effects on cleaned and irradiated BP films. While there are no significant differences due to irradiation, slight differences were observed as a result of methanol washing.

Table S2. Decomposition temperatures (TD) of BP*, BPIA*, BPIA, BPIM*, and BPIM

Temperature range (°C)	BP*	BPIA*	BPIA	BPIM*	BPIM
25 – 199	143.6	129.5	122.2	116.3	113.6
200 – 399	330.5	335.1	331.2	335.0	334.2
400 – 549	477.0	483.3	480.0	484.8	482.6
550 – 800	690.6	706.7	706.6	711.7	713.96

In conclusion, TGA results indicated that there were no significant changes due to irradiation (30 kGy), but notable differences were observed in relation to methanol washing, both before and during the grafting reaction.

(D) Determination of BP film composition from TGA

TGA was used to estimate the composition of the composite. This was achieved by interpolating stable temperatures between each decomposition on the Y-axis to obtain the weight percentage of the sample at those temperatures. The

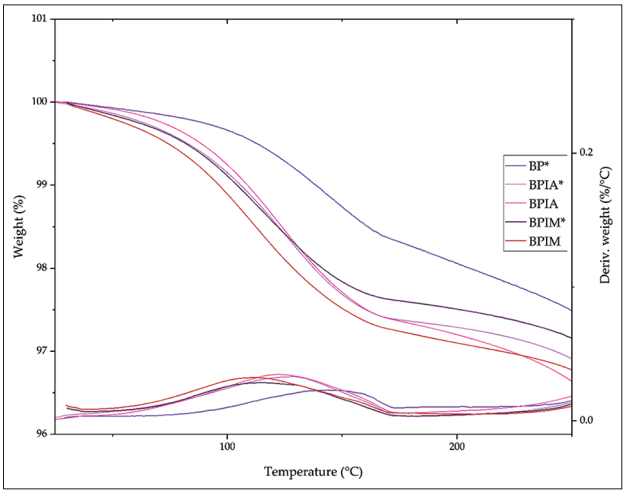

Figure S5. The first zone of thermograms (25 – 250°C), where the TD of pristine BP* was the higher. Water and volatile impurities begin to diminish around 100 – 150°C.

weight percent difference among each stable temperature corresponds to the individual composition.

First, the stable temperature of each plateau was determined, starting with the initial temperature (TA_0), the degradation temperatures (TD_1, TD_2, TD_3, and TD_4), and the final temperature measured (TA_4).

The initial plateau is denoted as TA_0, and the final as TA_4. To obtain the temperatures of the intermediate plateaus, the TDs are averaged (Equation SI). Then, three average temperatures (TA_n) are obtained (Table S3).

$$TA_n = \frac{TD + TD_{n+1}}{2}; n = 1,2,3 \quad \text{(SI)}$$

TA_0, TA_n, and TA_4 of each sample are interpolated with the weight percentage data (Table S4). Weight (%) and W_0, W_1, W_2, W_3, and W_4 are found (Table S5).

Finally, the weight (%) data between the plateaus are subtracted to obtain the net compositions by weight C_n (%) (Equation SII). The residue is then added to the four compositions obtained (Table S6).

$$C_n = W_{n-1} - W_n;\ n = 1,2,3,4 \quad \text{(SII)}$$

Table S3. The temperatures at weight loss of 10% and residue at 800°C of BP*, BPIA*, BPIA, BPIM*, and BPIM

Sample	Weight loss 10% (°C)	Residue at 800°C (weight%)
BP*	317.8	19.9
BPIA*	319.0	16.6
BPIA	318.2	18.2
BPIM*	320.1	16.5
BPIM	319.8	18.0

Table S4. TA_0, TA_1, TA_2, TA_3, and TA_4 of BP*, BPIA*, BPIA, BPIM*, and BPIM

T (°C)	BP*	BPIA*	BPIA	BPIM*	BPIM
TA_0	27.8	22.4	23.8	30.3	29.7
TA_1	237.1	232.3	226.7	225.7	223.9
TA_2	403.8	409.2	405.6	409.9	408.4
TA_3	583.8	595.0	593.3	598.3	598.3
TA_4	796.1	796.1	796.0	796.0	796.0

Table S5. W_0, W_1, W_2, W_3, and W_4 of BP*, BPIA*, BPIA, BPIM*, and BPIM

Weight (%)	BP*	BPIA*	BPIA	BPIM*	BPIM
W_0	100.0	100.0	100.0	100.0	100.0
W_1	97.7	97.1	97.0	97.4	97.0
W_2	75.9	73.5	74.3	74.1	75.4
W_3	30.5	27.3	29.22	27.0	29.0
W_4	19.9	16.6	18.2	16.5	18.0

Table S6. C_1, C_2, C_3, C_4, and residue of BP*, BPIA*, BPIA, BPIM*, and BPIM

Composition (%)	BP*	BPIA*	BPIA	BPIM*	BPIM
C_1 (impurities, plasticizer, and water)	2.3	2.9	3.0	2.6	3.0
C_2 (starch)	21.8	23.6	22.7	23.3	21.5
C_3 (aliphatic polyester)	45.4	46.2	45.0	47.1	46.4
C_4 (char and inorganic ashes)	10.6	10.7	11.0	10.5	11.0
Residue (mostly inorganic)	19.9	16.6	18.2	16.5	18.0