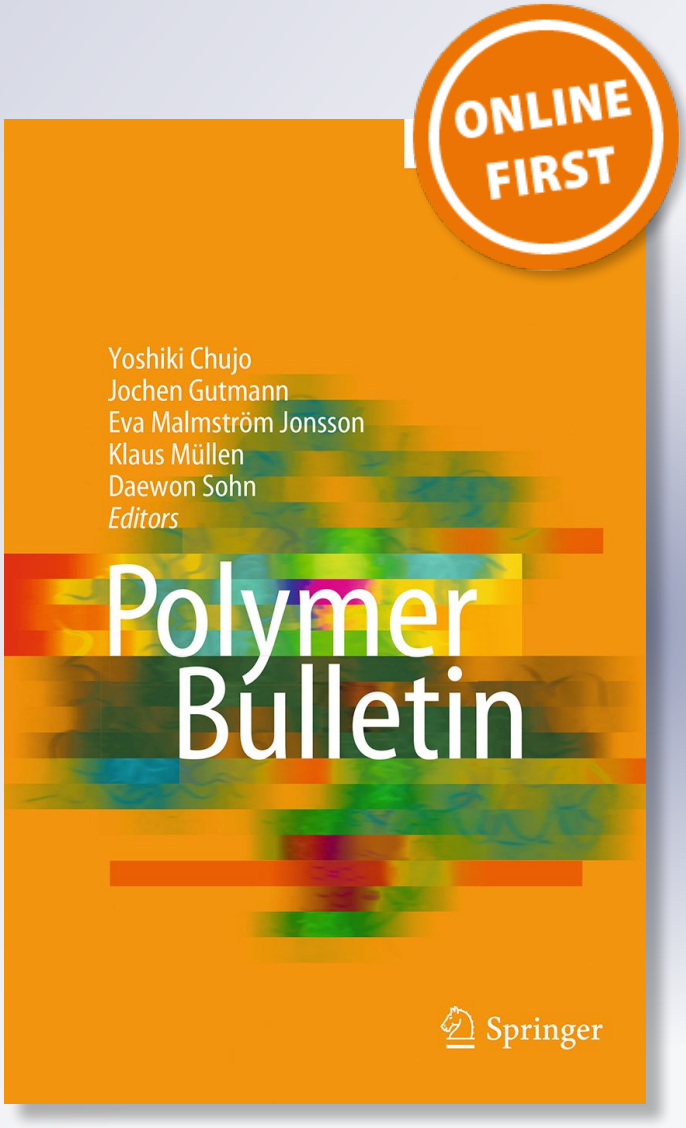
Study of mechanical, enzymatic degradation and antimicrobial properties of poly(butylene succinate)/pine-resin blends

Robert Chang, Roselyn Lata & David Rohindra

Polymer Bulletin

ISSN 0170-0839

Polym. Bull.
DOI 10.1007/s00289-019-02938-1



Springer

Polymer Bulletin
https://doi.org/10.1007/s00289-019-02938-1

ORIGINAL PAPER

Study of mechanical, enzymatic degradation and antimicrobial properties of poly(butylene succinate)/pine-resin blends

Robert Chang[1] · **Roselyn Lata**[1] · **David Rohindra**[1]

Received: 14 May 2019 / Revised: 10 August 2019 / Accepted: 27 August 2019

Abstract

Pine resin obtained from the plant (*Pinus Caribaea—Hondurensis*) was melt blended with poly(butylene succinate) (PBS) in mass ratios of the pine resin up to 50 wt%. The blends were tested for mechanical strength, melting and decomposition temperature and internal and spherulitic morphology using tensile test, differential scanning calorimetry, thermogravimetric analysis, scanning electron microscopy (SEM) and polarized microscopy, respectively. Enzymatic degradation of PBS and the pine-resin blends were investigated by porcine pancreatic and *candida rugosa* lipases while the antimicrobial property was studied against *Pseudomonas aeruginosa*, *Escherichia coli*, *Bacillus subtilis* and *Staphylococcus aureas* using the zone inhibition method. The two components were reported to be miscible and in blends with low pine resin, the thermal stability was similar to PBS. SEM micrographs showed homogeneity in the morphology of the blends. The mechanical properties of the blends showed a decrease in Young's modulus, but an improvement in flexibility was seen when compared to PBS. Enzymatic degradation was prominent in pine resin and blends containing pine-resin content but not with PBS. The pine resin was active against all the bacteria tested except *E. coli* while the blends were active against *P. aeruginosa* and *B. subtilis.*

Keywords Blends · Poly(butylene succinate) · Antimicrobial · Pine resin · Enzymatic degradation · Mechanical properties

✉ David Rohindra
rohindra_d@usp.ac.fj

[1] School of Biological and Chemical Sciences, Faculty of Science, Technology and Environment, University of the South Pacific, Private Mail Bag, Suva, Fiji

Published online: 30 August 2019

Introduction

Aliphatic polyesters are biodegradable because of their hydrolysable ester bonds. This property has generated significant interest in biodegradable polymers for applications in a variety of fields including medicine, agriculture and packaging. One of the most active areas of research in biodegradable polymers is the biomedical field, particularly in tissue engineering and drug delivery [1]. Recently, many researchers have been investing effort into modifying biodegradable polymers to make them more user-friendly, and into designing novel polymer blends out of naturally occurring materials [2]. The benefit of using natural materials is that some of the properties they possess which enables them to function in their natural environment are of interest to be incorporated into polymers through blending. A number of biological materials may be incorporated into synthetic biodegradable polymers, with the most common being starch and fibre extracted from various types of plants which are now used in the manufacture of many products. Specifically, several synthetic and natural biopolymers have been evaluated as implants or scaffolds for bone tissue engineering. The most widely investigated polymers includes poly(L-lactic acid) (PLLA), poly(glycolic acid) (PGA), polycaprolactone (PCL) and polybutylene succinate (PBS) [3, 4].

Poly(butylene succinate) is a biodegradable polyester which has been extensively researched for biomedical applications. PBS has a relatively high melting temperature ~ 114 °C, excellent processing properties and good thermal stability [5]. It is a succinic acid derivative from which it is polymerized and can be synthesized by numerous pathways [6]. However, PBS suffers from insufficient biocompatibility and bioactivity for medical applications and to overcome this limitation, researches have focused on modifying PBS through blending with other aliphatic polymers like poly(hydroxyl butyrate) and poly(ethylene oxide) [5] amongst others. Furthermore, the use of natural polymers to blend with biodegradable polymers is of utmost interest in biomedical applications due to its various advantages such as biocompatibility, no cytotoxicity concerns, biodegradability, and general recognition as safe [7, 8]. The capability of PBS to possess antimicrobial activity is limited, however, by blending with naturally or synthetic organic or inorganic compounds that show antimicrobial properties could be used for the development of antimicrobial polymeric materials that is non-toxic and safe to use. Polysaccharides, such as chitosan, cellulose, starch, pectin and carrageenan, have been used as it is or modified and blended with synthetic biopolymers to enhance the antimicrobial properties [9, 10].

However, many potential natural compounds with interesting properties are still underutilized and one such natural product is the gummy polysaccharide from the coniferous plant (*Pinus Caribaea—Hondurensis*). This resin [11] chiefly consisting of different resin acids especially abietic acid has been researched recently as the potential to produce "green plastics" [12].

Pine resin has been sourced for many years for industrial use, where distillation of the crude gum can result in gum rosin and turpentine substances. These have applications in the manufacturing of adhesives and fragrances, respectively,

to name a few [13]. The rosin component of the gum also has been previously utilized in the manufacturing of composites which are hydrophobic, the nature of which would be induced by the gum rosin component [14]. Apart from this, the literature on the usage of pine resin for polymer blends and systems is lacking. Thus, an opportunity arises by blending pine resin with polymers targeted towards biomedical applications. The anticipated use for the resin in this case would be to impart some of its properties to the blend so as to improve the properties of PBS, mainly in terms of physical ability.

This study is the continuation of investigations from our group on blending biodegradable polymers with the pine resin, where its properties were investigated [15, 16]. Previous work by our group on pine resin with PBS [15] found the system to be miscible. The focus of this study is to investigate the mechanical property, enzymatic and antimicrobial properties. The vision from this type of study is to implement antimicrobial property in materials used for manufacturing medical devices which are in fluid environments such as catheters. Currently, many patients with urinary dysfunction and who are on catheters frequently suffer from continuous bacterial infection especially *Pseudomonas aeruginosa*.

Experimental

Materials

Poly(butylene succinate) was purchased from Scientific Polymer Products Inc., with the melt flow index (MFI) of 39 g/10 min at 190 °C (under 2.16 kg weight force). The average molecular weight, M_w 78,000 g/mol and polydispersity index (PDI) of 1.78 was determined by GPC using polystyrene standards. The crude pine resin was extracted from the pine tree (*Pinus Caribaea—Hondurensis*). Any debris in the pine resin that got entrapped during extraction was removed by filtering the dichloromethane solution of pine resin. Dichloromethane (DCM) was used as the common solvent and was of analytical grade.

For degradation purposes, porcine pancreatic lipase and *Candida rugosa* lipase were purchased from Sigma-Aldrich Corporation. Buffer solutions were prepared from all analytical grade reagents, namely hydrous sodium dihydrogen phosphate ($NaH_2PO_4{\cdot}2H_2O$), anhydrous disodium hydrogen phosphate (Na_2HPO_4), sodium hydroxide (NaOH) and sodium azide (NaN_3) with distilled deionized water.

All other tests conducted involved physical manipulation of blended samples, without any further reagents used.

Blend preparation

PBS and the pine resin were weighed in varying amounts in the following ratios (PBS: pine resin): 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50 where the first value represents the PBS to make up a total weight of 4 g in each ratio. The contents were melt mixed in a reaction holder that was connected to a temperature

controller (Graseby Specac), and the temperature of the holder was controlled precisely to ± 0.5 °C. A mini-laboratory high shear mixer was used to melt mix at 50 rpm for 15 min at 125 °C. The pine gum was added to the molten PBS in small proportions during mixing to attain good distribution of the pine resin in PBS.

Differential scanning calorimetry

Thermal analysis was conducted on PBS and the blend samples using Perkin Elmer Pyris 6 DSC. About 8 mg of the sample was sealed in aluminium pans. The samples were heated to 140 °C at a heating rate of 10 °C/min and held for 2 min to remove thermal history. After being held for 2 min, the sample was quench cooled at a rate of 20 °C/min to the pre-set crystallization temperatures of 90, 85, 80 and 75 °C and isothermally crystallized for 24 h. The isothermally crystallized samples were heated at a heating rate of 10 °C/min to determine the melting temperature with nitrogen gas flowing at a rate of 20 mL/min. Indium was used to calibrate the DSC.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted on PBS, the pine resin and the blends using a thermogravimetric analyser (TA Q5000). 2 mg of the sample was heated from 25 to 500 °C at a heating rate of 2 °C min^{-1} in a nitrogen atmosphere.

Scanning electron microscopy

The internal morphology of the blends was observed using a SEM (JSM-5310LV, Joel, Tokyo, Japan). The samples were prepared in a form of a disc by melt pressing into a disc-shaped mould on a hot plate at 120 °C for 2 min under pressure of 50 kg/cm^2. The dimensions of the disc were 8.45 mm diameter and thickness of 1.55 mm. The mould after compressing was quench cooled in ice water. The dried sample discs were broken in liquid nitrogen and sputtered with gold onto the material to avoid accumulation of charges under the electron beam.

Polarized light microscopy

The spherulitic morphology of isothermally crystallized neat PBS, and the blends at 90, 85, 80 and 75 °C were observed under a Olympus Polarized Light Microscope equipped with a first-order retardation plate and a Nikon digital camera. Isothermal crystallization of neat PBS and the blends were done by melting a small portion of the sample on a glass slide and smearing with a cover slip. The spherulite morphology of the neat PBS and the blends were recorded at different isothermal crystallization temperatures.

Tensile testing

Mechanical properties of the blends were analysed in accordance with standards defined by International Standard ISO 527-2, for the determination of tensile properties of plastics (equivalent to ASTM D638).

The Shimadzu EZ Test Texture Analyser was used to observe the tensile properties of these samples, utilizing the "General Tensile Jig Set" accompanying the instrument. A downscaled size of the dumbbell mould shape given by the sample options in ISO 527-2 was selected due to the sample size capacity of the Shimadzu EZ Test Texture Analyser.

Samples were melted and hot-pressed at 125 °C into the mould which was pressed between two sheets of polyamide film under pressure of 50 kg/cm^2. Once the pressed samples had been crystallized by quench cooling, these were then placed onto the machine grips which were separated at a distance of 30 mm and the top grid pulled the sample upward at a speed of 5 mm/s till the sample strip broke. Five replicates of each sample were prepared and analysed. The elongation at break, tensile strength and elastic modulus were calculated.

Enzymatic degradation

PBS, the pine resin and the blends were subjected to enzymatic degradation by using two types of lipase, namely *Candida rugosa* and porcine pancreatic, for a total period of 20 days. Samples were prepared similar to that used for SEM except the mould size was $10 \times 10 \times 0.45$ mm. Once pressed, the mould containing the samples was quench cooled in ice water. The degradation experiment was carried out by placing four replicates of each sample in 10 mL of the degradation media which consisted of a phosphate buffer solution (0.05 M, pH 7.4) having a concentration of 1 mg/mL of lipase. Sodium azide was also added in proportions of 0.01% (wt/v) as a bacteriostatic agent. These were kept incubated at 37 °C for the 20-day period. At predetermined days, one sample was withdrawn from the media within the overall 20-day period. To maintain the activity of the lipase, fresh solutions were made for the degradation media to be changed daily. For comparison, neat PBS and the pine resin were analysed simultaneously with the blends. At each withdrawal, samples were rinsed with sterilized water, blotch dried, then dried further under vacuum at room temperature to remove excess moisture. Mass loss in comparison with the initial sample mass was recorded.

Antimicrobial testing

Antibacterial activity of PBS and pine-resin blends was investigated by zone inhibition method; method used in this study is similar to our previous study [16]. PBS and the blends were dissolved in dichloromethane (DCM) and loaded onto filter paper by dipping it into the solutions and the solvent was evaporated before testing. Briefly, four bacterial strains; *Escherichia coli* (*E. coli*) and *Pseudomonas*

aeruginosa (*P. aeruginosa*) (Gram negative bacteria), *Staphylococcus aureus* (*S. aureus*) and *Bacillus subtilis* (*B. subtilis*) (Gram positive bacteria) were used. For control, Gentamicin was used because this antibiotic was active against all the bacteria strains used in the test. On the nutrient agar plates, the filter paper containing the sample was placed, the bacteria inoculated and incubated for 24 h at 37 °C. The clear area surrounding the sample was the zone of inhibition.

Results and discussion

Blends of PBS and the pine resin were found to be miscible [15] which were determined through depression in equilibrium melting temperature and the presence of banding in the spherulites.

PBS was white in colour while the pine resin had a distinct yellowish colour. The blend had a synergetic effect of the colour from both the components and appeared visually homogenous. Figure 1 shows the variation in the colour of the samples.

Scanning electron microscopy

Pure and blend samples were broken in liquid nitrogen, and the internal morphology of the samples was viewed under the scanning electron microscope (SEM). The SEM micrographs of PBS, PBS 80 and PBS 50 are shown in Fig. 2a–c, respectively.

The internal morphology of neat PBS and the blends with high PBS content showed a rough surface while the blends with high pine resin were smooth. PBS 80 and PBS 90 (SEM images not included) showed similar rough morphology as that of neat PBS. Blends with higher pine resin PBS 50 and PBS 60 (SEM images not included) had similar smooth morphology. Homogenity between the two components was observed by the presence of smooth surface and no obvious phase separation.

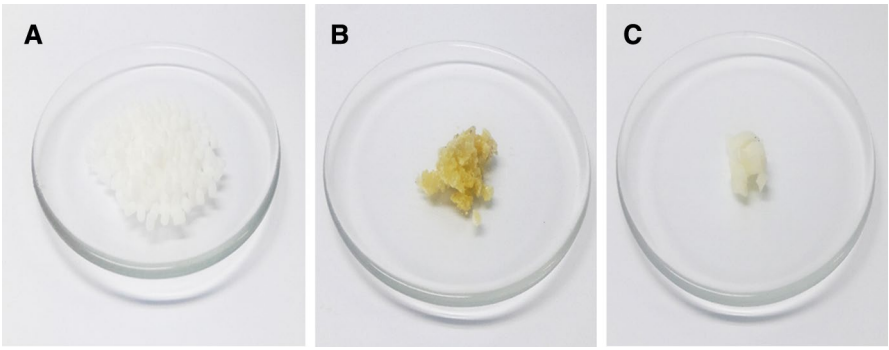


Fig. 1 Pure PBS (**a**), pine resin (**b**) and PBS 90 blend (**c**)

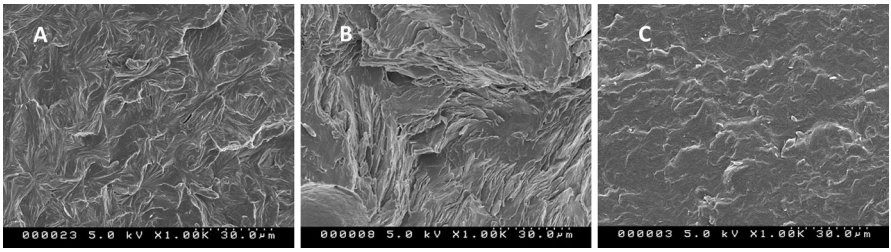


Fig. 2 SEM micrographs of PBS (**a**), PBS 80 (**b**) and PBS 50 (**c**)

Polarizing light microscopy

Spherulitic morphology has been successfully used to show miscibility in blends by the presence of extinction rings when thermal methods have failed. Miscibility in blends of poly(caprolactone)/poly(vinyl formal) and poly(caprolactone)/hydroxyl ethyl cellulose acetate has been shown by the presence of extinction rings in the spherulites [17, 18]. Figure 3 shows the spherulites of neat PBS and the blends after isothermal crystallization at 90 °C. Spherulites of neat PBS exhibited negative birefringence and as the composition of pine resin increased in the blends the emergence of the extinction rings in the spherulites became more obvious. The presence of extinction rings is a clear indication of miscibility. Keith and Padan [19] explained

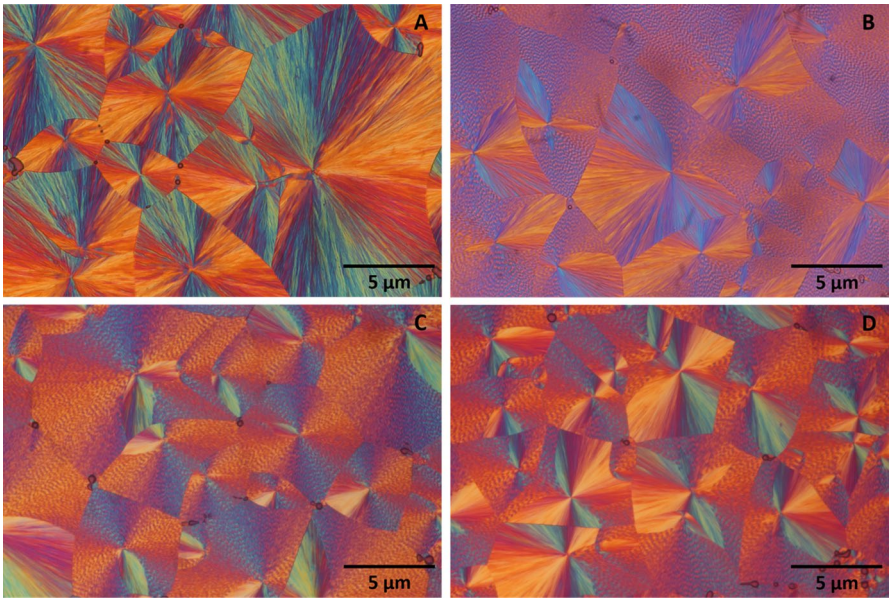


Fig. 3 Micrographs from polarized light microscopy of PBS (**a**), PBS 90 (**b**), PBS 80 (**c**), PBS 70 (**d**) blend isothermally crystallized at 90 °C

this behaviour in blends on the basis of the lamellar twisting model. The crystalline lamellar of PBS tends to twist reducing the fold surface energy as the pine resin increases in the interlamellar region of PBS. The saturation by the pine resin in the interlamellar region tends to twist the PBS chains during folding.

Thermal properties

Figure 4 shows the thermal stability of PBS, pine resin and the blends as analysed by thermogravimetric method. A two-stage degradation mechanism is observed. A small decrease in the mass for PBS started around 250 °C followed by a sharp decrease at 350 °C. The first step is due to auto-catalysis and the second mechanism is due to the nth-order reaction [20]. On the other hand, the pine resin showed low thermal stability. It started degrading considerably at around 130 °C and slowed down at around 300 °C. Blends with high percentage of PBS (PBS 90 and PBS 80) showed the degradation profile similar to PBS but the degradation started at a lower temperature of 200 °C. Interestingly, the addition of small amounts of pine resin to PBS did not decrease the thermal stability of the blends significantly. With increasing pine resin in the blends (PBS 70 and PBS 60), two-step degradation becomes evident. The first significant decrease in the blends is for the degradation of the pine resin at around 230 °C and also due to the auto-catalysis of PBS followed by the second degradation at 350 °C due to the nth-order degradation of PBS. To avoid crowding, the TGA profiles of PBS 90 and PBS 70 have been omitted because their profiles were similar to PBS 80 and PBS 60, respectively. The degradation temperature for pine resin in the blends was not affected much.

Miscibility between PBS and pine resin at different blend ratios was analysed by DSC. Blends that have both components as amorphous will show miscibility by a single composition-dependent glass transition temperature while blends that have

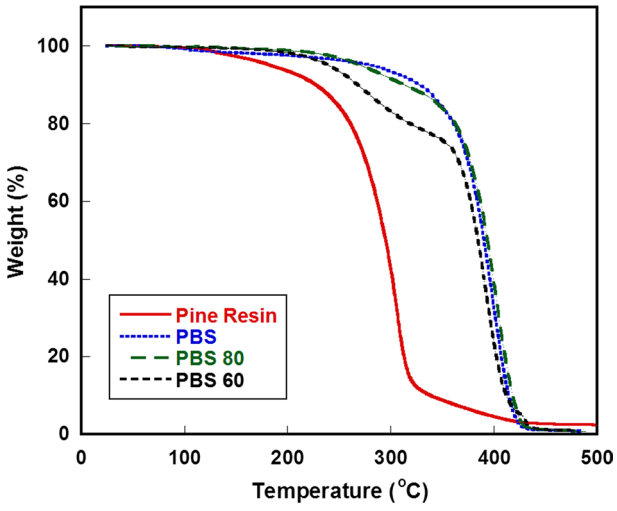


Fig. 4 Thermogravimetric profile of Pine resin, PBS and the blends

one component as crystalline will show a depression in equilibrium melting temperature (T_m^o). The thermograms of isothermal-crystallized PBS and the blends obtained at a heating rate of 10 °C/min are shown in Fig. 5a.

The isothermally crystallized PBS showed multiple melting peaks and has been reported to originate due to melting-crystallization and remelting process [21]. The linear Hoffman–Weeks plot was used to determine the (T_m^o) of PBS and the blends using the first melting endotherm as it was found to be directly dependent on the crystallization temperature. The theory related to this method is well defined in the literature [22]. The Hoffman–Weeks plot of PBS and the blends are shown in Fig. 5b. The experimental (T_m^o) for PBS of 134.5 °C in this study is in good agreement with the reported value of 135 °C [23]. Miscibility in crystalline/amorphous blend system is determined by a depression in the (T_m^o) of the crystalline component according to Nishi–Wang expression [24]. The depression in (T_m^o) of PBS was found to be dependent on the pine-resin content and this indicated the miscibility of PBS with pine resin.

Mechanical properties

Figure 6 shows stress–strain tests to ascertain the mechanical properties. The tensile strength, elongation at break and elastic modulus are given in Table 1. The strength of PBS is notably higher than the blends, while there is a decrease in strength with the addition of the pine resin. The elastic (Young's) modulus changes in a similar manner. The elongation at break, however, as seen in Fig. 6 increases with the addition of pine resin up to 30% and then decreases for higher pine-resin composition.

By comparing the curves, blends with less pine gum show more elongation and ductility than PBS. The strain-hardening effect and extended elongation was found to be the highest in PBS 70 blend. The percentage of pine resin in the PBS 70 blend could have given the optimum rearrangement of the polymer chains to be arranged in an orderly manner that allowed more elasticity in the blend.

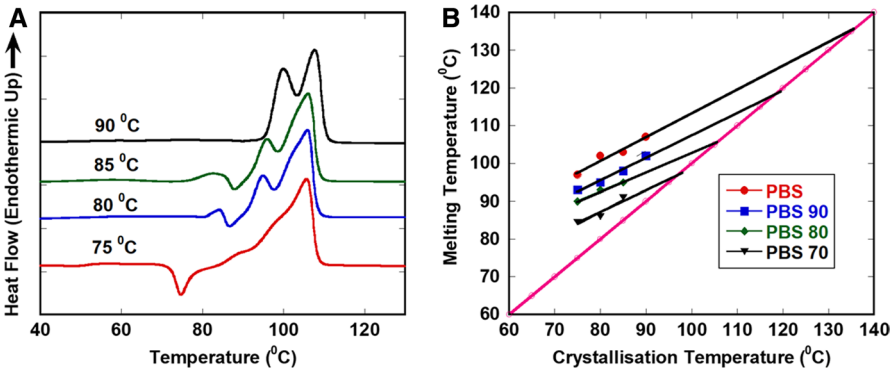


Fig. 5 Melting endotherms of isothermally crystallized PBS (**a**), Hoffman–Weeks plot of PBS and PBS pine-resin blends (**b**)

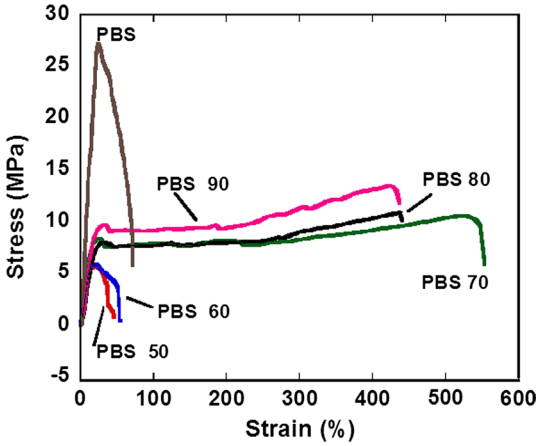


Fig. 6 Stress–strain curves of PBS and PBS/pine-resin blends

Table 1 Mechanical properties of PBS and PBS/pine-resin blends

Blend	Elastic modulus (MPa)	Tensile strength (N)	Strain at break (%)
PBS	17.8	81.5	25
PBS 90	6.4	40.4	427
PBS 80	5.2	32.8	441
PBS 70	7.1	31.7	513
PBS 60	5.7	17.7	51
PBS 50	8.3	16.8	29

In contrast, blends up to 30% of the pine resin were found to exhibit improved elongation than neat PBS. However, blends with higher percentage of pine resin (> 40%) showed a rather different behaviour in comparison with both the neat PBS and those with a lesser percentage of pine resin. The strain-hardening effect and extended elongation is absent. This could be due to the excess pine-resin hindering the rearrangement process of the polymer chains to an orderly fashion after necking had occurred, hence creating weak points which may have caused the sample to break early.

Enzymatic degradation

Gravimetric analysis of PBS, pure pine resin, and selected PBS blends (PBS 80 and PBS 50) were conducted after degradation. Mass loss by degradation was recorded in each sample for different time intervals by porcine pancreatic lipase and *Candida rugosa* lipase as shown in Fig. 7a, b, respectively.

Pine resin, in both porcine pancreatic and *Candida rugosa* lipases, degraded the most during the incubation period; PBS, however, did not. PBS has been known to

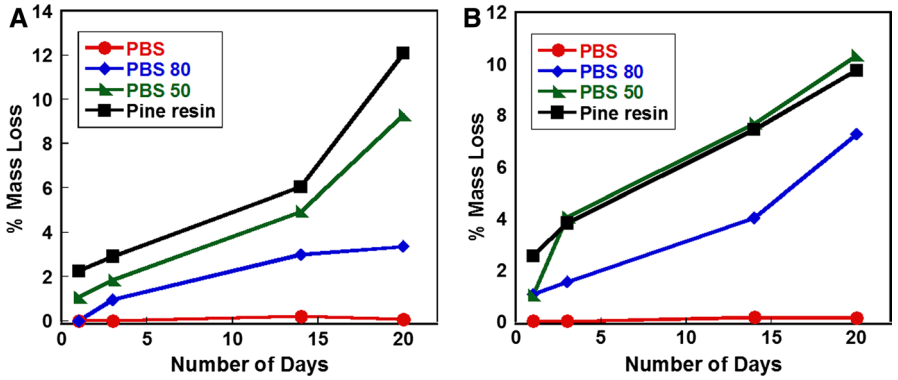


Fig. 7 Weight loss of neat and blend samples in porcine pancreatic (**a**) and *Candida rugosa* (**b**) lipase enzymes

degrade in other lipase enzymes of different origin, such as PS lipase-*Pseudomonas cepacia* and *Candida cylindracea* lipase amongst others [25–27].

PBS 80 and PBS 50 blends show an increasing degradation pattern in both porcine pancreatic and *Candida rugosa* lipases with increasing pine-resin content. By the end of the incubation period, PBS 50 is seen to have lost more mass relative to pure pine resin, as well as the other samples. This does in fact suggest that the decomposition of the PBS blends is due in large part to the ability of the pine resin to degrade, since the pure PBS did not degrade in the selected media.

Figure 8 shows the SEM images of the internal morphology of PBS (Fig. 8a) and the blends after 20 days of degradation in porcine pancreatic lipase. The presence of holes (Fig. 8b, c) is indicative of degradation. Similar morphology was observed in samples degraded by *Candida rugosa* lipase.

Antimicrobial test

The antibacterial activity of the pine resin, PBS and the blends were tested against four bacterial strains, *Pseudomonas aeruginosa*, *Escherichia coli*, *Bacillus subtilis*

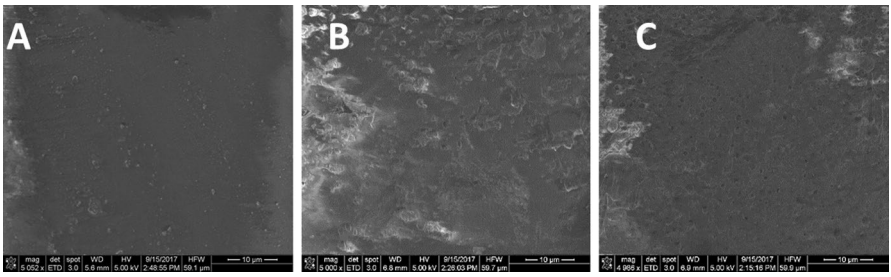


Fig. 8 The SEM images of PBS (**a**), PBS 80 (**b**) and PBS 50 (**c**) after 20 days of degradation with porcine pancreatic lipase

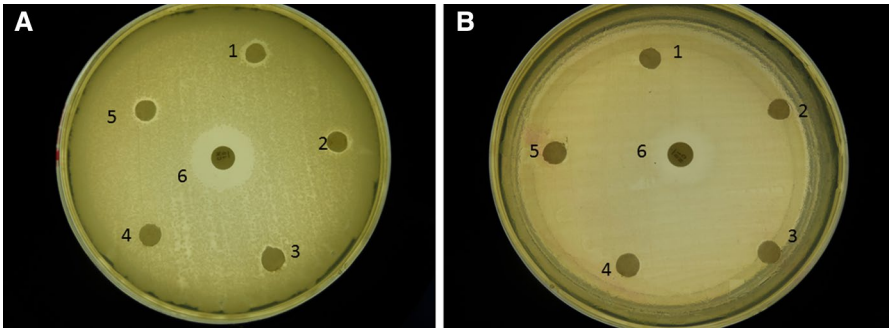


Fig. 9 Agar plates showing zone of inhibition for pine resin (1), PBS 80 (2), PBS (3), DCM (4), PBS 50 (5) and gentamicin (6) for bacterial strains of *Bacillus subtilis* (**a**) and *Escherichia coli* (**b**)

Table 2 Zone of inhibition of pine resin, PBS and blends against four bacterial strains

Blend	*P. aeruginosa* (mm)	*E. coli* (mm)	*S. aureus* (mm)	*B. subtilis* (mm)
PBS	0	0	0	0
PBS 80	4.3	0	0	6
PBS 50	8.3	0	0	7
Pine resin	8	0	7	8.7
Gentamicin	23.7	23.7	25.3	21.3
DCM	0	0	0	0

and *Staphylococcus aureus* by observing the presence and absence of inhibition zones (IZ) on agar plates as shown in Fig. 9. The zone of inhibition by Gentamicin was consistent against the four bacterial strains tested, and the inhibition zones by the pine resin, neat PBS and the blends against the four bacterial strains are shown in Table 2.

The Activity Index (AI) was used to express the effectiveness of the blends in inhibiting the bacteria relative to the effectiveness of a commercial drug sample, Gentamicin [28]. Activity Index (AI) is defined according to Eq. 1.

$$\mathrm{AI} = \frac{\text{IZ of sample}}{\text{IZ of Gentamicin}} \tag{1}$$

where IZ is the inhibition zone in mm

Here IZ of sample is of the test sample divided by the IZ of the commercial sample (Gentamicin). The commercial sample Gentamicin exhibits an index of 1 (or 100%). The (IZ) obtained for Gentamicin trials were within the range of expected values/standards [29].

Figure 10 shows the antibacterial activity index of PBS, the pine resin and the blends tested against the four strains of bacteria. Pine resin was found to be active against all the bacterial strains except *E. coli*, whereas PBS was inactive with

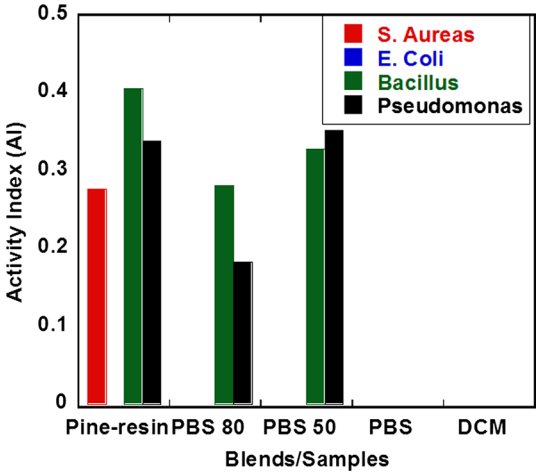


Fig. 10 Antimicrobial activity of PBS, pine resin and selected blends in four bacterial strains

all the bacterial strain. In the blends, the antimicrobial activity against *P aeruginosa* and *B subtilis* was fairly similar to the pine resin; however, it was not active against *S. aureus* and *E. coli*. This could probably be due to the chemical compounds present in the pine resin active against *S. aureus* being miscible with PBS through interactions and the resultant effect was that there was lack of diffusion of this antibacterial chemical to the surrounding agar in order for it to create an inhibition zone on the agar plate (Fig. 9).

Recently, there have been reports of antibacterial property in polymers due to nanostructured topology through the fabrication of polymer surfaces with nanoimprint lithography [30]. However, for this blend system SEM images showed smooth surface, thus topological effect is ruled out. Antibacterial property is due to the pine resin.

Conclusion

Miscible blends of PBS and pine resin were prepared by melt mixing different mass ratios up to 50 wt% and investigated for mechanical properties, thermal stability, enzymatic degradation and antimicrobial properties. SEM images showed a homogenous internal surface indicating no phase separation. Degradation by porcine pancreatic and *Candida rugosa* lipase showed selective degradation of the pine resin in the blends and the degree of degradation increased with increasing pine resin in the blend. Although pine resin was active against *Pseudomonas aeruginosa*, *Bacillus subtilis* and *Staphylococcus aureus*, the blends were active against the former two only. The use of natural compounds that are active against *Pseudomonas aeruginosa* in the development of medical devices such as catheters is an interesting area for further investigation with other polymer systems.

Acknowledgements The authors acknowledge the funding provided by The University of the South Pacific Research Committee (Grant No. F3106-FST12-001).

References

1. Kumar A, Karthick K, Arumugam KP (2011) Biodegradable polymers and its applications. Int J Biosci Biochem Bioinf 1:173–176
2. Al-Rawajfeh AE, Al-Salah HA, Al-Rhael I (2006) Miscibility, crystallinity and morphology of polymer blends of polyamide-6/poly (β-hydroxybutyrate). Jordan J Chem 1:155–170
3. Ciardelli G, Chiono V, Vozzi G, Pracella M, Ahluwalia A, Barbani N, Cristallini C, Giusti P (2005) Blends of poly-(epsilon-caprolactone) and polysaccharides in tissue engineering applications. Biomacromolecules 6:1961–1976
4. Sarasam A, Madihally SV (2005) Characterization of chitosan–polycaprolactone blends for tissue engineering applications. Biomaterials 26:5500–5508
5. Zaverl M, Valerio O, Misra M, Mohanty A (2015) Study of the effect of processing conditions on the co-injection of PBS/PBAT and PTT/PBT blends for parts with increased bio-content. J Appl Polym Sci 133:41278. https://doi.org/10.1002/app.41278
6. Xu J, Guo BH (2010) Poly(butylene succinate) and its copolymers: research, development and industrialization. Biotechnol J 5:1149–1163
7. Chavalitpanya K, Phattanarudee S (2013) Poly(lactic acid)/polycaprolactone blends compatibilized with block copolymer. Energy Proc 34:542–548
8. Ma P, Cai X, Wang W, Duan F, Shi D, Lemstra PJ (2014) Crystallization behavior of partially crosslinked poly(beta-hydroxyalkonates)/poly(butylene succinate) blends. J Appl Polym Sci 131:41020. https://doi.org/10.1002/app.41020
9. Álvarez-Paino M, Muñoz-Bonilla A, Fernández-Garcìa M (2017) Antimicrobial polymers in the nano-world. Nanomaterials 48:1–44
10. Muñoz-Bonilla A, Echeverria C, Sonseca Á, Arrieta MP, Fernández-Garcìa M (2019) Bio-based polymers with antimicrobial properties towards sustainable development. Materials 12:641
11. Have R, Teunissen PJ (2001) Oxidative mechanisms involved in lignin degradation by white-rot fungi. Chem Rev 101:3397–3413
12. Adler E (1957) Structural elements of lignin. Ind Eng Chem 49:1377–1383
13. Di Maggio J (2014) In Callison Pacific pine chemicals LLC. In: PCA international conference, Seattle Washington
14. Wang J, Yao K, Korich AL, Li S, Ma S, Ploehn HJ, Iovine PM, Wang C, Chu F, Tang C (2011) Combining renewable gum rosin and lignin: towards hydrophobic polymer composites by controlled polymerization. J Polym Sci A Polym Chem 49:3728–3738
15. Chang R, Lata R, Rohindra D (2017) Miscibility study of poly(butylene succinate) and pine-gum blends. Key Eng Mater 735:148–152
16. Chang R, Rohindra D, Lata R, Kuboyama K, Ougizawa T (2019) Development of poly(ε-caprolactone)/pine resin blends: study of thermal, mechanical and antimicrobial properties. Polym Eng Sci 59:E32–E41
17. Rohindra D (2009) Miscibility determination in poly(ε-caprolactone)/poly(vinyl formal) blend by equilibrium melting temperature and spherulite morphology. J Macromol Sci Phys B 48:1103–1113
18. Xiao Q, Yan S, Rogausch KD, Petermann J, Huang Y (2001) Ring-banded spherulites poly(ε-caprolactone) blended with hydroxyethyl cellulose acetate as an indication for partial miscibility. J Appl Polym Sci 80:1681–1686
19. Keith HD, Padden FJ (1984) Twisting orientation and the role of transient states in polymer crystallization. Polymer 25:28–42
20. Chrissafis K, Paraskevopoulos KM, Bikiaris DN (2005) Thermal degradation mechanism of poly(ethylene succinate) and poly(butylene succinate): comparative study. Thermochim Acta 435:142–150
21. Rohindra D, Kuboyama K, Ougizawa T (2010) High pressure analysis of the multiple melting endotherms of poly(ethylene succinate) and poly(butylene succinate). J Macromol Sci B 49:470–478
22. Hoffman JD, Miller RL (1997) Kinetic of crystallization from the melt and chain folding in polyethylene fractions revisited: theory and experiment. Polymer 38:3151–3212

23. Yoo ES, Im SS (1999) Melting behavior of poly(butylene succinate) during heating scan by DSC. J Polym Sci B 37:1357–1366
24. Nishi T, Wang TT (1975) Melting point depression and kinetic effects of cooling on crystallization in poly(vinylidene fluoride)-poly(methyl methacrylate) mixtures. Macromolecules 8:909–915
25. Lee CW, Kimura Y, Chung J (2008) Mechanism of Enzymatic degradation of poly(butylene succinate). Macromol Res 16:358–651
26. Nikolic MS, Djonlagic J (2001) Synthesis and characterization of biodegradable poly(butylene succinate-co-butylene adipates). Polym Degrad Stab 74:263–270
27. Thirunavukarasu K, Purushothaman S, Sridevi J, Aarthy M, Gowthaman MK, Nakajima-Kambe T, Kamini NR (2016) Degradation of poly(butylene succinate) and poly(butylene) succinate-co-adipate) by a lipase from Yeast Cryptococcus sp. grown on agro-industrial residues. Int Biodeterior Biodegrad 110:99–107
28. Singh G, Kumar P (2013) Phytochemical study and screening for antimicrobial activity of flavonoids of *Euphorbia hirta*. Int J Appl Basic Med Res 3:111–116
29. Comuzzi B, Arcelloni C, Vaiani R, Paroni J (2001) Gentamicin diffusion in Mueller–Hinton agar plates from different manufacturers. J Antimicrob Chemother 47:496–498
30. Nerantzaki M, Kchagias N, Francone A, Fernandez A, Torres CMS, Papi R, Papadopoulou TC, Bikiaris DN (2018) Design of a multifunctional nanoengineered PLLA surface by maximizing the synergies between biochemical and surface design bactericidal effects. ACS Omega 3:1509–1521