Optimization of process parameters of microwave processed PLLA/coir composites for enhanced mechanical behavior

Manoj Kumar Singh¹, Nishant Verma² and Sunny Zafar³

¹,²,³School of Engineering, IIT Mandi, VPO Kamand, Mandi, Himachal Pradesh 175005, INDIA
d16058@students.iitmmandi.ac.in

Abstract. In the present work, poly-L-lactide (PLLA)/coir-based polymer composites were fabricated by a novel manufacturing route of microwave processing. Microwave processing is faster and cleaner process as compare to conventional manufacturing processes. The effect of microwave temperature, time and fibre weight reinforcement was evaluated for their mechanical behaviour using uniaxial tension and flexural tests. The full factorial design was used to optimize the process parameters for enhanced mechanical performance of the composites. The analysis of results was done on Design Expert V.10 software. PLLA/coir composite processed at 140 °C for 12 min having fibre weight percentage of 30% has maximum tensile strength of 18 MPa. The maximum flexural strength 48 MPa reported was for the same specimen having maximum tensile strength. The optimized value of process parameters obtained was, processing temperature: 140°C, time 12 min and coir reinforcement percentage of 30%. The fractured specimens were characterised using scanning electron microscopy to support the results.

1. Introduction

Natural fibre reinforced bio-composites have great potential for wide material applications owing to their eco-friendliness. The growing trends are toward the development of light weight, high strength with cost effective and environment sustainable materials [1]. Now-a-days synthetic fibres are replaced with natural fibres because of low cost and environmentally friendly nature. The various type of natural fibers are jute, kenaf, wood residues, sisal, ramie, flax, pineapple leaf and coir [1]. Among the natural fiber coir fiber is low cost and widely used in industrial applications. Coir is obtained from coconut trees which are found in tropical region i.e. Indonesia, India, Sri Lanka, Brazil etc.

The processing of polymers composite generally done by conventional heating methods but nowadays microwave processing is becoming an emerging technology [2]. The microwave processing is different than conventional thermal processing. The microwave processing has certain advantages as compare to conventional processing like selective heating, volumetric heating, quick start and stop, reduction of processing time, saving energy and environment friendly [3]. In current scenario the industries of thermoplastic are shifted toward cost effective engineering composite by use different kinds of fibers.

There are different types of polymer matrix are available in the market i.e. polyethylene (PE), polypropylene (PP), polycaprolactone (PCL), polyhydroxybutyrate (PHB), polylactic acid (PLA) etc. Many studies have been done on the potential application of natural fibres to make polymer composites but just few studies have been done on the possibilities to use renewable polymer i.e. PLA, PHB [4]. Poly-L-lactic acid (PLLA) is the most promising material among the different biodegradable polymers because of its tendency to easily biological attack [1]. Since PLLA is ecofriendly in nature and can easily be converted into compost, PLLA are highly in demand for various applications where recyclability is difficult. Though PLLA has many advantages but it has some limitations like brittleness, hygroscopic nature. To reduce the brittleness and increase the tensile strength different plasticizers are used i.e. triacetin, glycerol etc. [5]

The progress in PLLA polymer can be seen from the detailed literature discussed below. Okhsman et al. checked the feasibility of polylactic acid (PLA) with natural fibres as reinforcement for the composites [4]. They find that composite strength is about 50% better as compared to similar PP/flax fibre composites used for automobile panel. Also, the addition of plasticizer doesn’t have major effect. Suryanegara et al. studied the effect of crystallization of PLA on the thermal and mechanical properties of micro-fibrillated cellulose-reinforced PLA composites [5]. And they find that by increasing the micro
fibrillated cellulose (MFC) content in both amorphous and crystallized states, the tensile modulus and strength of neat PLA were improved. Peltola et al. studied the wood based PLA and PP composites and check the effect of matrix and fibre type [6]. They concluded that the wood fibres have higher plastic reinforcement than wood flour. Thermomechanical pulping (TMP) fibres provided the highest enhancement in mechanical properties in polylactic acid composites with uniform fibre dispersion as compared to wood fibre.

The detailed scrutiny of literature review shows the there is no work done on optimization of process parameters of microwave processed PLLA/coir composites for mechanical behavior. Therefore the objective of this study shows the effect of microwave temperature, processing time and wt. % of coir fibre on mechanical properties of PLLA/coir composite using full factorial technique [7].

2. Material and Method

2.1. Raw materials
In the present work, high-performance grade of poly-L-lactide (PLLA) was used as the matrix material in form of pellets. The PLLA pellets were supplied by Synbra Technology, Netherlands. Coir were obtained from Go Green Products, Chennai, India.

2.2. Fabrication of composite
Natural fibres are hydrophobic in nature because of presence of wax and non-cellulosic particles. For better interfacial adhesion between natural fibre (coir) and PLLA matrix, the wettability of coir fibre should be better. To increase the wettability of the coir fibre surface treatment had been done as done by different researchers[8]. In present research work 10% NaOH solution has used for surface treatment of coir fibre. After alkali treatment coir fibre were chopped manually having the length in the range of 5-10 mm. These chopped fibres were spread manually in an alumina mould and pressed to achieve uniform thickness mat.

Owing to the hygroscopic nature of PLLA pellets, they were dried in a hot air oven (Make: Macro Scientific Works; Model: OUT-125) at 65°C for 8 h prior to processing. These pre weighted PLLA pellets were put into alumina mould of size 9 × 2.2 × 1 cm³ and placed in a domestic multimode microwave applicator (Make: LG, India; Model: MC2886BRUM) to obtain PLLA sheet. After obtaining the PLLA sheet of size 9 × 2.2 × 0.1 cm³ the coir mat and PLLA sheets was stacked layer wise and processed within the microwave applicator. For proper adhesion between the coir mat and PLLA sheets pressure was applied with the help of dead weight. The applied pressure should be adequate in such a way that the material will not come outside the alumina mould during processing and no pores will appear in the composite. Finally, microwave processed laminated composite is obtained. In the present work, three parameters were taken i.e. temperature, time and fibre wt. %. Different composites were fabricated according to the full factorial design generated by design expert software along with sample code as shown in table 1. The stepwise fabrication process of coir/PLLA composites through microwave processing is shown in figure 1.

| Exp. No. | Temperature (°C) | Time (min) | Fibre (Wt. %) | Specimen code |
|----------|------------------|------------|---------------|---------------|
| 1        | 160              | 8          | 30            | S1            |
| 2        | 140              | 8          | 10            | S2            |
| 3        | 140              | 8          | 30            | S3            |
| 4        | 160              | 12         | 30            | S4            |
| 5        | 140              | 12         | 30            | S5            |
| 6        | 160              | 8          | 10            | S6            |
| 7        | 140              | 12         | 10            | S7            |
| 8        | 160              | 12         | 10            | S8            |
Figure 1. A stepwise process for fabrication of microwave-processed PLLA/coir composites

3. Mechanical Testing and Characterization
The specimens were conditioned at 25 °C for 12 h before mechanical testing. ASTM D3039 and ASTM D790 standard was followed to perform the tensile test and flexural test, respectively of microwave processed PLLA/coir composites. Both tests were carried out on a universal testing machine (Make: Tinius Olsen, United Kingdom, Model: H50KS), having uniform extension rate of 1 mm/ min. To ensure repeatability of the test data five specimens of each type of composites were tested. SEM (Make-FEI, USA; Model- NOVA 450) was used to assess the mechanisms of failure in the tensile fractured specimens.

4. Results and Discussion
The obtained results of responses are shown in table 2. The obtained results are analyzed using Design Expert V.10 software.

| Specimen code | S1  | S2  | S3  | S4  | S5  | S6  | S7  | S8  |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Tensile strength (MPa) | 17.5±1 | 14±1 | 15±1 | 16.8±1 | 18±1 | 16.5±1 | 16±1 | 15.5±1 |
| Flexural strength (MPa) | 44±2.5 | 39±2 | 40±2 | 42±2.5 | 48±2.5 | 40±2 | 35±2 | 32.5±2 |

4.1. Tensile Strength
Figure 2(a) shows the bar graph of tensile tested composites. Specimen S5 shows the maximum tensile strength of 18 MPa, which is 28.57 % greater than the S2 composite. From the figure 2(a) it is observed that as the fibre wt. % increases the tensile strength increases. The effect of processing temperature shows the proportionality trend in tensile strength at constant time of 8 min whereas at the processing time of 12 min inverse trend was obtained. The reason behind this may be at lower temperature the
The dipole oscillation moment is lower. Due to this the relaxation time for the dipole oscillation will increase and the interfacial bonding between the PLLA and fibre will increases. The above result can also be justified with help of SEM fractographs shown in figure 2(b) and (c). Figure 2(b) shows the SEM image of tensile fractured specimen processed at 140 °C for 12 min and the coir reinforcement of 30%. From figure 2(b), it can be seen that the interfacial bonding between the coir fibre and PLLA matrix is good therefore the tensile strength will increase. Figure 2(c) shows the SEM image of tensile fractured specimen, microwave-processed at 140 °C for 8 min with fibre reinforcement of 30 wt. %. From figure 2(b) it is observed that there is poor bonding between the fibre and the PLLA matrix.

4.1.1. Analysis of tensile strength

The 2FI (2 factor interaction) model was selected for analysis. Power transformation was used to make data fitting in model in which $y' = (y+k)^\lambda$, where $\lambda = -1.61$ and $k = 0$. The values of $\lambda$ and $k$ were used for data fitting in model. The selected model was validated by Analysis of Variances (ANOVA) tests. Table 3 presents the ANOVA table for tensile strength. The $p$ value is 0.0008 which indicates the significant model. The significant model terms are $A$, $B$, $C$, $A*B$, $B*C$, $C*A$. There are reasonable agreements between adjacent $R^2$ and predicted $R^2$. Adeq Precision measures the Signal to noise ratio. This ratio must be greater than 4. The selected model has 3014.18 Adeq Precision. This represents the adequate signal and model can be used to navigate the design space.

| Source       | Sum of Squares | dof | Mean Square | F Value | Prob > F | $p$-value | % contribution |
|--------------|----------------|-----|-------------|---------|----------|-----------|----------------|
| Model        | 1.699E-5       | 6   | 2.832E-6    | 9.970E+5 | 0.0008   | significant |
| A-temperature| 2.425E-6       | 1   | 2.425E-6    | 8.536E+5 | 0.0007   | 14.27     |
| B-Time       | 2.179E-6       | 1   | 2.179E-6    | 7.671E+5 | 0.0007   | 12.82     |
| C-wt.% of coir | 4.434E-6     | 1   | 4.434E-6    | 1.561E+6 | 0.0005   | 26.09     |
| AB           | 7.705E-6       | 1   | 7.705E-6    | 2.713E+6 | 0.0004   | 45.35     |
| AC           | 1.316E-7       | 1   | 1.316E-7    | 46319.54 | 0.0030   | 0.77      |
| BC           | 1.180E-7       | 1   | 1.180E-7    | 41548.32 | 0.0031   | 0.69      |
| Residual     | 2.841E-12      | 1   | 2.841E-12   |         |          |           |
| Cor Total    | 1.699E-5       | 7   |             |         |          |           |

**R Squared** = 1.000
**Adj R squared** = 1.000
**Pred R squared** = 1.000
**Adeq Precision** = 3014.18

Figure 3. Predicted vs actual plots for tensile strength
The regression equation for tensile strength is shown in Eq. (1). The regression equation for tensile strength is plotted by diagnosis plots. The predicted vs actual plots are shown in Figure 3. The predicted vs actual plot shows that the predicated values and actual values are approaching to each other.

\[
\text{(Tensile Strength)}^{1.61} = 0.0918 - 5.201E-004 \times \text{temperature} - 7.74288 \times 10^{-3} \times \text{Time} + 2.060E-004 \times \text{wt.} \% \text{ of coir} + 4.9069E-005 \times \text{temperature} \times \text{Time} - 1.2824E-006 \times \text{temperature} \times \text{wt.} \% \text{ of coir} + 6.072E-006 \times \text{Time} \times \text{wt.} \% \text{ of coir}.
\]

4.1.2 Effect of combined interactions

Figure 4(a) shows the combined interaction of microwave processing temperature and time on tensile strength. This observation was done by keeping wt.% of coir at 20%. It is observed that tensile strength was more affected by processing time up to the temperature of 147°C beyond this temperature the tensile strength is less affected by processing time. Figure 4(b) shows the combined effect of wt. % of coir and temperature on tensile strength. This observation was taken at constant time of 10 min. It is shown that the tensile strength is increasing with increase in wt.% of coir up to the temperature range of 147°C. After 147-155 °C there is no considerable change in the tensile strength. At temperature 160 °C the tensile strength decreases with increase in wt.% of reinforcement, this may be due to the decomposition of coir fibre at higher temperature. Figure 4(c) shows the combined interaction of wt.% of coir and time on tensile strength. It was observed from figure 4(c) that there is negligible affect of wt.% of coir on tensile strength up to the processing time 11 min and after 11 min the tensile strength starts decreasing with increase in wt.% of coir fibre.
Figure 4. Combined effect plots for (a) Temperature and time vs Tensile strength (b) wt.% of coir and temperature vs tensile strength (c) wt.% of coir and time vs tensile strength

4.2. Flexural strength

Figure 5 shows the flexural strength of different composites processed with the help of microwave. These composites were fabricated at different temperature, time and fibre reinforcement percentage. There are different combinations of above discussed parameter are used for the composite fabrication, which are modelled using design expert software. The maximum flexural strength was reported on S5 which was processed 140 °C for 12 min and the coir reinforcement of 30%. The minimum flexural strength of 32.5 MPa was obtained in sample S8. This may be due to the over processing temperature of the composite and lesser fibre reinforcement (10 wt. %).

Figure 5. Flexural strength of various microwave-processed composites

4.2.1. Analysis of flexural strength

The 2FI model was selected for modelling of flexural strength data. The model was validated by ANOVA. The power transformation was used for proper fitting of data in the model. The value of $\lambda$ and $k$ was -0.3 and -0.1, respectively. The p value for selected model is 0.496, which is less than 0.05. The
significant model terms present in ANOVA table 4 are A, B, C, A*B, A*C, B*C. The Adeq Precision is 47.35 in this case, which is desirable for model. The difference between Adj R² and Predicted R² is less than 0.2, which indicates that the model can be used to make the prediction of data.

Table 4. ANOVA result for Flexural Strength

| Source         | Sum of Squares | dof | Mean Square | F Value | p-value | Prob > F | % contribution |
|----------------|----------------|-----|-------------|---------|---------|----------|----------------|
| Model          | 3.002E-10      | 6   | 5.003E-11   | 238.17  | 0.0496  | significant |
| A-temperature  | 3.384E-12      | 1   | 3.384E-12   | 16.11   | 0.1554  | 1.13      |
| B-Time         | 2.936E-11      | 1   | 2.936E-11   | 139.77  | 0.0537  | 9.77      |
| C-wt.% of coir | 1.567E-10      | 1   | 1.567E-10   | 745.77  | 0.0233  | 52.15     |
| AB             | 3.019E-11      | 1   | 3.019E-11   | 143.71  | 0.0530  | 10.05     |
| AC             | 2.059E-12      | 1   | 2.059E-12   | 9.80    | 0.1968  | 0.69      |
| BC             | 7.852E-11      | 1   | 7.852E-11   | 373.83  | 0.0329  | 26.14     |
| Residual       | 2.101E-13      | 1   | 2.101E-13   |         |         |           |

R-Squared - 0.99 Adj R-Squared - 0.995 Pred R-Squared - 0.955 Adeq Precision - 47.35

The regression equation for flexural strength is shown in eq. (2). The regression equation for flexural strength is plotted by diagnosis plots. The predicted vs actual plots are shown in figure 6. The predicted vs actual plot shows that the predicated values and actual values are approaching to each other.

(Flexural Strength - 0.10)² = 1.056E-004 × 8.047E-007 × temperature -1.047E-005 × Time + 1.884E-006 × wt.% of coir + 9.712E-008 × temperature × Time -5.0733E-009 × temperature × wt.% of coir - 1.566E-007 × Time × wt.% of coir

(2)

Figure 6. Predicted vs actual plots for flexural strength

4.2.2 Effect of combined interactions

Figure 7(a) shows the combined effect of time and temperature on flexural strength at constant wt.% of coir, i.e. 20%. The considerable change in flexural strength was observed at 160°C and at processing
time of 10 min. Figure 7(b) shows the combined effect of wt.% of coir and temperature on flexural strength at constant time of 10 min. It is observed that there is considerable increase in flexural strength after 15 wt.% of coir fibre at all temperature ranges. Figure 7(c) shows the combined effect of coir and processing time on flexural strength. The negligible change is observed by increase in wt.% of coir fibre upto 10 min of processing time. From 10-12 min of processing time, the flexural strength starts increasing with increase in wt. % of reinforcement.

![Figure 7](image)

**Figure 7.** Combined effect plots for (a) Temperature and time vs Flexural strength (b) wt.% of coir and temperature vs Flexural strength (c) wt.% of coir and time vs Flexural strength

### 4.3. Optimization of responses

The optimization is done to maximize the desirable variable and minimize the undesirable variable. In the present investigation there are two responses, tensile strength and flexural strength. The criteria for optimization is present in table 5.

| Parameters               | Goal         | Lower limit | Upper limit | Lower weight | Upper weight | Importance |
|--------------------------|--------------|-------------|-------------|--------------|--------------|------------|
| Temperature              | In range     | 140         | 160         | 1            | 1            | 3          |
| Processing time          | In range     | 8           | 12          | 1            | 1            | 3          |
| wt.% of reinforcement    | In range     | 10          | 30          | 1            | 1            | 3          |
| Tensile Strength         | Maximize     | 14          | 18          | 1            | 1            | 5          |
| Flexural Strength        | Maximize     | 32.5        | 48          | 1            | 1            | 5          |

The solution obtained is expressed in desirability ramp plots in figure 8. The optimized values of temperature time and wt.% of coir are 140 °C, 12 min and 30% respectively.
5. Conclusions

- The PLLA/Coir composites were successfully fabricated by microwave processing.
- Sample S5 has maximum tensile and flexural strength of 18 MPa and 48 MPa, respectively.
- SEM fractographs reveals that the sample S5 has better interfacial adhesion as compare to S2.
- The combined effect of temperature and time is more on tensile strength as compare to other input parameters.
- The flexural strength is mostly influenced by wt.% of coir fibre.
- The optimized parameters for maximum tensile and flexural strength are 12°C, 12 min. and 30 wt. % coir reinforcement.

References

[1] Ibrahim N A, Md Zin Wan Yunus W, Othman M, Abdan K and Hadithon K A 2010 Poly(Lactic Acid) (PLA)-reinforced kenaf bast fiber composites: The effect of triacetin J. Reinf. Plast. Compos. 29 1099–111
[2] Manoj Kumar Singh and Sunny Zafar 2018 Development and mechanical characterisation of microwave-cured thermoplastic based natural fibre reinforced composites J. Thermoplast. Compos. Mater.
[3] Singh M K and Zafar S 2018 Influence of microwave power on mechanical properties of microwave-cured polyethylene/coir composites J. Nat. Fibers 00 1–16
[4] Oksman K, Skrifvars M and Selin J-F 2003 Natural fibres as reinforcement in polylactic acid (PLA) composites Compos. Sci. Technol. 63 1317–24
[5] Suryanegara L, Nakagaito A N and Yano H 2009 The effect of crystallization of PLA on the thermal and mechanical properties of microfibrillated cellulose-reinforced PLA composites Compos. Sci. Technol. 69 1187–92
[6] Peltola H, Pääkkönen E, Jetsu P and Heinemann S 2014 Composites : Part A Wood based PLA and PP composites : Effect of fibre type and matrix polymer on fibre morphology , dispersion and composite properties Compos. Part A 61 13–22
[7] Verma N and Vettivel S C 2018 Characterization and experimental analysis of boron carbide and rice husk ash reinforced AA7075 aluminium alloy hybrid composite J. Alloys Compd. 741 981–998
[8] Sumi S, Unnikrishnan N and Mathew L 2017 Surface Modification of Coir Fibers for Extended Hydrophobicity and Antimicrobial Property for Possible Geotextile Application J. Nat. Fibers 14 335–45