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Influence of processing parameters on the impact strength of biocomposites: A statistical approach

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ABSTRACT

Injection molded biocomposites from a new biodegradable polymer blend based matrix system and miscanthus natural fibers were successfully fabricated and characterized. The blend matrix, a 40:60 wt % blend of poly(butylene adipate-co-terephthalate), PBAT and poly(butylene succinate), PBS was chosen based on their required engineering properties for the targeted biocomposite uses. A big scientific challenge of biocomposites is in improving impact strength within the desired tensile and flexural properties. The stiffness–toughness balance is one of the biggest scientific hurdles in natural fiber composites. Thus, the key aspect of the present study was in investigating an in-depth statistical approach on influence of melt processing parameters on the impact strength of the biocomposite. A full factorial experimental design was used to predict the statistically significant variables on the impact strength of the PBS/PBAT/miscanthus biocomposites. Among the selected processing parameters, fiber length has a most significant effect on the impact strength of the biocomposites.

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1. Introduction

The increasing environmental pollution throughout the world has placed great emphasis on eco-friendly sustainable material development. Consequently, more attention has been focused on a sustainable material development by using bio-based and/or biodegradable materials instead of petroleum based non-biodegradable materials. Governments in many countries are supporting the usage of green products, and a reduction of dependence on petroleum because of the associated environmental benefits [1]. Currently there are many bioplastics (biodegradable and/or bio-based polymers) available in the market. Among them, PBS and PBAT are promising biodegradable polyesters. The impact toughness/strength of the PBS is insufficient for a wide range of applications [2]. Blending PBS with PBAT can enhance the impact and tensile toughness of the PBS [3]. However, these polymers still cannot be used for wide range of applications on their own because they cannot fulfill some of the product requirements [4]. These issues can be overcome by blending, reinforcing, and forming composites with inexpensive natural fibers in the polymer matrix [1].

Natural fiber (kenaf, flax, hemp and jute) reinforced composites have been used for many applications including those in the automotive, electronic, horticultural, packaging, consumer goods and construction sectors [5]. Miscanthus is an alternative fiber for viable biocomposite applications. Miscanthus is a typical lignocellulosic C4 perennial grass and is a promising non-food crop which grows rapidly compared to some other crops. There are many advantages of utilizing miscanthus as reinforcement in composites such as high yield [6], low moisture content at harvest [6], low input conditions [7], soil remediation potential [7], good fiber properties (tensile strength, hardness, and modulus) [8], and thermal stability up to 200 °C [9]. Currently, miscanthus fibers have only limited applications though these could be diversified by developing viable biocomposites. The key strategy is the combination of bioplastics with miscanthus fibers which could create an eco-friendly sustainable biocomposite. Recently, the performance of miscanthus fibers reinforced in a biodegradable polymer matrix has been investigated by few researchers [6–8,10–13]. In order to compare the effect of miscanthus fibers on the resulting composites, Nagarajan et al. [12] investigated the performance of five different lignocellulosic fibers (miscanthus, switchgrass, wheat straw, soy stalk and corn stalk) reinforced poly(hydroxybutyrate-co-valerate) PHBV/PBAT (45/55 wt%) composites. This study revealed that the miscanthus fiber reinforced PHBV/PBAT composites exhibited superior properties compared to other fiber reinforced PHBV/PBAT

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composites. Similar observations were made in the miscanthus fibers reinforced PHBV/polylactide (PLA) (60/40 wt%) composites [7]. A recent study by Zhang et al. [11] reported that the toughened multiphase green composite can be obtained from miscanthus fiber reinforced PHBV/PBAT/epoxidized natural rubber (ENR) matrix.

In a multi-phase material, processing parameters and variables play a vital role in the performance of the resulting material. Recently, many researchers conducted experimental studies to investigate the performance of heterogeneous composite materials. Johnson et al. [13] used a two-level factorial design to investigate the influence of processing parameters such as temperature, screw speed, filler content, and size on the impact performance of Mater-Bi®/miscanthus composites. In another study [6] a Box–Cox transformation method was used to examine the influence of processing parameters on the performance of the Mater-Bi®/miscanthus fiber composites. From these studies it was noted that processing temperature has more influence on the performance of the composites. The significant influences of processing parameters (processing temperature, screw speed, humidity, filler content, and the aspect ratio of filler) on the elastic modulus, heat deflection temperature and impact strength of the Mater-Bi®/wood flour composites has been studied by Morreale et al. [14]. The selected processing variables are based on specific industrial target applications including automotive indoor furnishing and panels. The filler aspect ratio had more influence on the impact strength while filler content exhibited more influence on the heat deflection temperature as well as the elastic modulus. Another study by Kirwan et al. [5] studied the influence of processing parameters on the flexural properties of poly(vinyl alcohol), PVA/poly(vinyl acetate), PVAc/miscanthus composites. The authors found that the processing temperature to be the most influencing factor on the flexural properties followed by the washing of fibers.

Most studies in current literature investigate the composites (short fiber reinforced biodegradable polymer blend matrix based composites) characteristics with fixed processing parameters. The aim of this work was to fabricate biocomposites using a bioplastic blend of PBS/PBAT (60/40 wt%) as the matrix and miscanthus fibers as the reinforcement with several independent processing variables (processing temperature, screw speed, holding pressure, and fiber length). The influence of the processing variables on the performance of the biocomposites was investigated by using a statistical approach, *i.e.*, full factorial design and analysis of variance (ANOVA).

2. Full factorial design methodology

More than one factor can affect an experimental result. In general, a factorial experiment studies the simultaneous effects of two or more factors on experimental results [15]. In the literature, it was suggested that there are many independently controllable processing parameters/factors (processing temperature, mixing speed, pressure, reinforcement amount, and size of the reinforcement) which influence the performance of the resulting biocomposite [6,13,14]. As such, a detailed investigation was conducted to fix the upper and lower limits of the independent processing parameters for PBS/PBAT/miscanthus composites fabrication. The miscanthus fibers can be melted and compounded with polymers at up to 200 °C without exhibiting any major thermal decomposition [6]. As a result the miscanthus fiber reinforced composites preparation should be performed below said temperature. Shear force occurs during the extrusion process and can damage the fiber geometry. The mixing speed or screw speed of the composites can play a vital role in maintaining sufficient fiber geometry (aspect ratio). For instance, high screw speed may cause more fiber breakage while low screw speed can lead to less homogeneity of the components in the composites. In this study miscanthus is used as a short fiber which should have a wide range of aspect ratio distributions. This work aims to study the effect of two different fiber lengths (2.07 and 4.65 mm) on the mechanical performance of the composites. One of the hypothesis that was tested in this work is that high holding pressure will lead to a composite with higher performance. High holding pressure may also help to reduce the shrinkage of the resulting composites.

Table 1
Selected processing parameters and their respected levels.

S. No.	Factor	Notation	Lower level	Higher level
1	Temperature (°C)	*A*	140	180
2	Holding pressure (bar)	*B*	6	10
3	Screw speed (rpm)	*C*	100	150
4	Fiber length (mm)	*D*	2	4

The processing temperature, fiber length, holding pressure and screw speed were selected to be the variables in the factorial design. Two levels were assigned for each of these parameters for the composite fabrication as shown in Table 1. These parameter levels were selected after a series of screening experiments had been conducted. In order to fully understand the interaction between the parameters, a full factorial design was selected in a 2^k experimental design. In this study, randomization was carried out to increase the precision of the experimental results by reducing the sampling variability. It was assumed that the experimental results between the two levels are linear. The experimental design was performed in statistical software MINITAB®17 and, the same software was used to analyze the results by means of statistical plots (main effect plot, interaction effect plot, normal probability plot, residual plots, and Pareto plot) at a 95% confidence level.

3. Materials

PBS and PBAT were obtained from Xinfu pharmaceuticals Co. Ltd, China. Both PBS and PBAT are semi-crystalline grade produced from fossil fuel based monomers. The PBS and PBAT have onset thermal degradation temperatures of 372 and 377 °C, respectively [16]. Two different lengths (2.08 ± 0.95 and 4.65 ± 2.45 mm) of miscanthus fiber were kindly supplied by New Energy Farms, Ontario, Canada. Hereafter, these two fiber lengths (2.08 ± 0.95 and 4.65 ± 2.45 mm) will be referred as 2 and 4 mm. The storage moisture of the miscanthus fiber and polymer was 7.16 ± 0.16% and 0.29 ± 0.04%, respectively at room temperature. In this study, all the materials were used without any further purification.

4. Experimental procedure

4.1. Samples preparation

Based on our previous study [16], we have selected a PBS/PBAT (60/40 wt%) blend as an optimum composition for composites fabrication. Hereafter, the PBS/PBAT (60/40 wt%) blend will be referred to as PBS/PBAT blend. Table 2 shows some of the general properties of miscanthus fibers and PBS/PBAT blend. A 30 wt% miscanthus fiber is selected to fabricate biocomposites with a blend of biodegradable polymer (PBS/PBAT) matrix. The choice of using miscanthus fiber in this present work was because of its good fiber properties and the strong potential supply. Prior to melt compounding, both polymers and miscanthus fibers were dried at 80 °C for at least 12 h. This 12 h hot air oven drying was sufficient enough to reach a constant moisture content which was 2.29 ± 0.27% for fiber and 0.1 ± 0.03% for polymers. Appropriate

Table 2
Physical and mechanical properties of the PBS/PBAT blend and miscanthus fibers.

Properties	Values
Melt flow index of PBS/PBAT (60/40 wt%) blend	33 ± 3 g/10 min (190 °C with 2.16 kg)
Notched Izod impact strength of PBS/PBAT (60/40 wt%) blend	Non-break [3]
Onset thermal degradation of miscanthus fiber[a]	~260 °C
Density of the miscanthus fibers	1.41 g/cm^3 [7]
Modulus of the miscanthus fibers	9.49 GPa [8]

[a] measured by thermogravimetric analysis (TGA) with a heating rate of 20 °C/min under nitrogen atmosphere.

amounts of dried polymers and fibers were manually pre-mixed at the solid state and the composites fabrication was performed by changing four processing variables, as shown in Table 3. The PBS/PBAT/miscanthus fiber composites were prepared in a lab-scale extrusion and injection molding process. The lab-scale co-rotating twin screw extruder (DSM explore®, Netherlands) and injection molding machine (DSM explore®, Netherlands) had volume of 15 and 12 cm^3, respectively. The composite samples were molded with a mold temperature of 30 °C and the residence time of the materials inside the extrusion barrel was 2 min.

4.2. Characterization methods

4.2.1. Fiber dimension measurement

In order to measure the fiber length after processing, the composite samples were dissolved in chloroform and then fibers were isolated by filtering. The isolated fibers were rinsed thoroughly with the same solvent and dried at 70 °C for 24 h. The processed and unprocessed fibers were photographed through a digital camera (Nikon AF-S DX) and the fiber dimensions were measured by Image J software (at least 85 individual fibers were measured). The measured fibers length was inserted in Minitab®17 statistical software to get fiber length distribution histogram.

4.2.2. Mechanical testing and scanning electron microscopy (SEM)

All the prepared test specimens were conditioned at room temperature for at least 40 h before evaluating mechanical performances. Universal Testing Machine (Instron, Model-3382) was used to measure the flexural and tensile properties of the test samples in accordance with ASTM D790 and ASTM D638, respectively. The flexural testing was performed with a cross-head speed of 14 mm/min. The tensile properties of neat PBS/PBAT blend matrix and all the composite samples were measured with a cross-head speed of 50 and 5 mm/min, respectively. Notched Izod impact testing was performed according to ASTM D256 in a TMI monitor impact testing machine using a 5 ft lb pendulum. The impact test specimens had a dimension of 64 mm (length) × 12.7 mm (width) × 3.2 mm (thickness). The reported tensile and flexural properties are averages of five samples for each formulation. Minimum six test samples were tested for each formulation and the average values are reported for impact strength. The morphologies of the fracture surface were observed by using a SEM (Inspect S50-FEI SEM). Prior to observation of the sample morphology; the samples were sputter-coated with a thin layer of gold.

5. Results and discussion

5.1. Mechanical properties

Table 3 represents the mechanical properties of biocomposites as well as the factors that are used for each experiment. Due to the reinforcing effect of miscanthus fibers, the flexural strengths of all the composites were higher than that of the neat PBS/PBAT blend (denoted as control). A similar trend has been observed in the PHBV/PBAT/miscanthus composites and rubber toughened PHBV/PBAT/miscanthus fiber composites [11,12]. Kirwan et al. [5] have found improved flexural properties of miscanthus fiber reinforced PVA/PVAc blend. Due to strong reinforcing capability of miscanthus fibers, both tensile and flexural modulus of the composites increased (data not shown) compared to neat PBS/PBAT blend. On the other hand, all the composites showed inferior tensile strength as compared to the control sample (matrix). The observed reduction is attributed to the incompatibility between the miscanthus fiber and the PBS/PBAT blend matrix. Such a reduction is very often observed in natural fiber reinforced thermoplastic composites [7]. The miscanthus fibers have higher wax and silica content compared to wood fibers which may be responsible for the incompatibility between the PBS/PBAT matrix and the miscanthus fibers [13]. The tensile and flexural strengths of the PBS/PBAT/miscanthus composites are not significantly affected with varying processing parameters. Similarly, tensile and flexural modulus of the PBS/PBAT/miscanthus composites was not affected significantly with varying processing parameters (data not shown). The Izod impact strength of the control sample (matrix) showed

Table 3
A complete summary of all the experiments and the related mechanical properties of PBS/PBAT/miscanthus composites.

Experiment	Temperature (°C)	Screw speed (rpm)	Holding pressure (bar)	Fiber length (mm)	Tensile strength (MPa)	Flexural strength (MPa)	Impact strength (J/m)
1	140	100	10	2	21.9 ± 0.26	37.48 ± 0.23	82.34 ± 4.55
2	140	150	10	4	18.8 ± 0.34	34.62 ± 0.30	66.45 ± 3.50
3	180	150	6	2	19.9 ± 0.30	38.61 ± 0.66	76.48 ± 7.85
4	180	100	6	2	19.4 ± 0.34	37.57 ± 0.62	77.04 ± 3.16
5	180	100	6	4	21.6 ± 0.54	39.08 ± 0.43	62.94 ± 2.70
6	180	150	10	2	20.7 ± 1.13	37.86 ± 0.92	67.17 ± 3.08
7	180	100	10	2	19.8 ± 0.40	36.96 ± 2.08	70.90 ± 2.85
8	140	150	10	2	21.1 ± 0.41	37.62 ± 0.27	79.29 ± 6.10
9	140	150	6	4	19.0 ± 0.43	34.62 ± 0.70	67.00 ± 3.13
10	140	150	6	2	19.6 ± 1.05	34.72 ± 0.83	75.39 ± 3.50
11	140	100	6	4	19.3 ± 0.49	33.93 ± 0.35	70.93 ± 3.00
12	180	100	10	4	19.8 ± 0.81	33.99 ± 0.50	67.89 ± 5.00
13	140	100	10	4	19.2 ± 0.55	34.51 ± 0.68	68.19 ± 4.51
14	180	150	6	4	21.6 ± 0.18	38.74 ± 0.92	62.57 ± 4.37
15	180	150	10	4	19.7 ± 0.76	34.39 ± 0.16	62.76 ± 3.79
16	140	100	6	2	19.7 ± 0.67	34.89 ± 1.24	77.55 ± 2.95
Control	140	100	6	0	32.9 ± 1.24	17.12 ± 0.27	Non-break

non-break behavior under tested impact conditions. Contrastingly, all composite samples showed hinge break behavior under the selected test conditions. This phenomenon was attributed to the incorporation of stiff fibers into a ductile polymer matrix. Taking this into consideration, the observed impact strength of the PBS/PBAT/miscanthus composites was still superior to carbon fiber reinforced composites such as PLA/carbon fiber (70/30 wt%) [17], PHBV/carbon fiber (70/30 wt%) [18], poly (trimethylene terephthalate), PTT/carbon fiber composites (70/30 wt%) [19]. It can be noted that the processing parameters have more influenced on the impact strength of PBS/PBAT/miscanthus composites.

5.2. Analysis of variance (ANOVA) for impact strength

ANOVA is a statistical model, which can be used to investigate the significant main and interaction effects of factors with respect to response. The model had 15 degrees of freedom with four factors and two levels. To estimate the individual and interaction factors upon the impact strength, sum of square (SS), mean square (MS), *F*-test statistics and *P*-values are presented in the ANOVA Table 4. In this study we have used an alpha level (α) = 0.05 for each *F* test to analyze the factorial design experiment. Usually, the higher value of *F*-ratio suggests more influence of that factor on the experiment response. According to an *F*-test, $F = 25.61$ has a *P*-value of 0.004. Since the *P*-value is less than 0.05, we then have sufficient evidence to conclude that the mean impact strength of the biocomposites was significantly influenced by fiber length. At a 95% confidence interval ($P < 0.05$), it should be noted that the screw speed and holding pressure do not show significant effects on the impact strength of the composites. The interaction effects did not significantly influence the impact strength of the composites. The square correlation coefficient (R^2) was used to judge the adequacy of the developed model fit. The R^2 value can be interpreted as the percentage reduction in the total variation in the experiment obtained by using the developed model. The typical R^2 value is $0 \leqslant R^2 \leqslant 1$. The value of R^2 (87.78%) and R^2_{adj} (63.35%) is substantial and hence the developed model fits the experimental results very well.

5.3. Effect of processing parameters on the impact strength

Among the mechanical properties, impact strength was more affected by the processing factors than other mechanical properties. The impact strength of the short fiber composites mainly influenced by many factors including matrix intrinsic properties, optimum fiber–matrix interaction, fiber concentration, fiber geometry, fiber–matrix stress transfer efficiency, fiber orientation, and fiber dispersion and distribution [20]. At the same time, the fiber bridging, fiber pull-outs, crack propagation and matrix deformation mechanisms contribute a vital role in the impact rupture of short fiber reinforced composites [21]. Many of these mechanisms contribute simultaneously during impact tests which make it complicated to determine the impact strength of the composites. Therefore, it is important to investigate the statistically significant factors upon the impact performance. Morreale et al. [14] have studied the impact performance of the composites with varying processing parameters. In addition, John et al. [6,13] have performed a systematic study of impact performance of Mater-Bi®/miscanthus composites by using factorial design.

In the present study, the effect of processing parameters/factors on the notched Izod impact strength was statistically analyzed. More specifically, the statistical analysis was mainly focused on determining which factors and interactions parameters had more influence on the Izod impact energy of the biocomposites. Generally, the plot which provides a response with respect to the changes in the levels of the factors is called the main effect plot. Fig. 1 shows the influence of the investigated factors on the impact strength of the resulting biocomposites. Factors with steeper slopes have larger effects and thus a greater influence on the results. From the main effect plots, it can be observed that the temperature and fiber length factor levels have more significant effect which is evidenced with a strong line slope. On the other hand, holding pressure has almost no effect on the response when varying its levels. The composites prepared with low temperature processing (140 °C), low screw speed (100 rpm), and small fiber length (2 mm) have higher impact strength compared to those produced with high processing temperature (180 °C), high screw speed (150 rpm) and high fiber length (4 mm). The holding pressure did not have a great effect on the impact strength upon changing levels such as 6 and 10 bar.

Fig. 2 represents the statistically significant binary interaction between the selected variables. The joint effects of two factors such as fiber length/holding pressure, fiber length/screw speed, holding pressure/screw speed, fiber length/temperature, holding pressure/temperature, and screw speed/temperature were investigated. If there was no interaction between the selected variables, the lines on the display should have been approximately parallel. When the response of two factors was not parallel this indicates a possible interaction between the selected factors. Among the selected variable combinations, it can be noted that the most significant interaction variables are holding pressure/temperature, fiber length/temperature, screw speed/holding pressure, and fiber length/holding pressure. There is no significant interaction between the temperature/screw speed and screw speed/holding pressure on the impact strength of the resulting biocomposites. It can be concluded that the selected variable combinations (temper-

Table 4
Analysis of variance (ANOVA) for notched Izod impact strength.

Source	*DF*	Sum of squares (SS)	Mean squares (MS)	*F*	*P*
Temperature	1	96.97	96.97	6.63	0.050
Screw speed	1	26.70	26.70	1.82	0.235
Holding pressure	1	1.51	1.51	0.10	0.761
Fiber length	1	374.71	374.71	25.61	0.004
Temperature * screw speed	1	0.07	0.07	0.01	0.946
Temperature * holding pressure	1	15.43	15.43	1.05	0.352
Temperature * fiber length	1	2.70	2.70	0.18	0.686
Screw speed * holding pressure	1	2.75	2.75	0.19	0.683
Screw speed * fiber length	1	0.17	0.17	0.01	0.917
Holding pressure * fiber length	1	4.63	4.63	0.32	0.598
Error	5	73.16	14.63		
Total	15	598.81			

S = 3.82523; R-Sq = 87.78%; R-Sq(adj) = 63.35%.

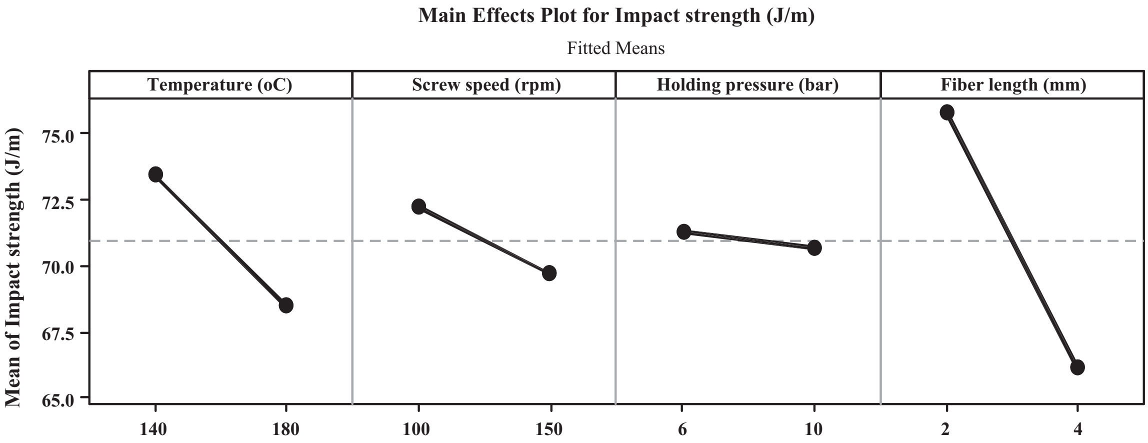

Fig. 1. Main effect plot for the impact strength of PBS/PBAT biocomposites.

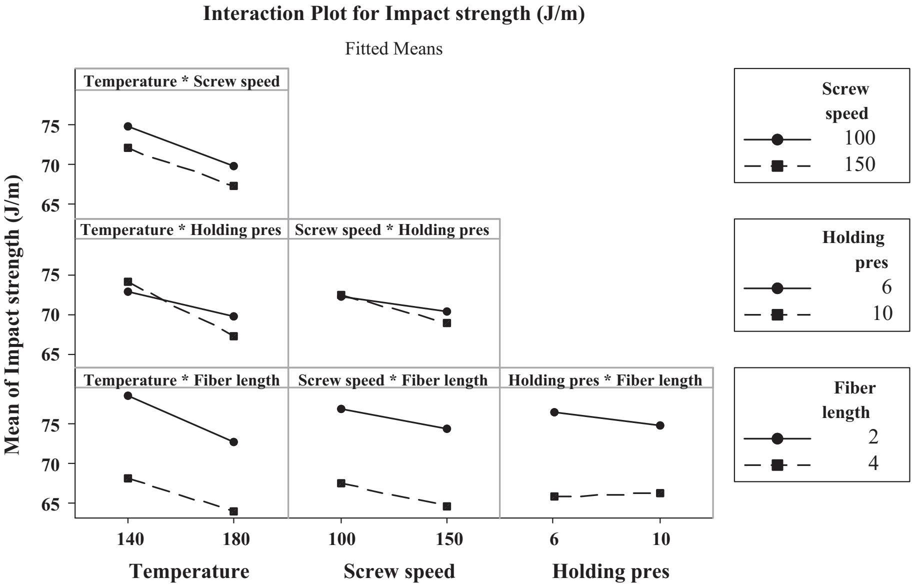

Fig. 2. Plot of interaction effects for the impact strength of PBS/PBAT biocomposites.

ature/screw speed and screw speed/fiber length) behave separately, which are not dependent on each other. Out of the selected four variables the fiber length had the most significant effect on impact strength while screw speed had the least significant effect.

Fig. 3 shows the significant factors influencing the impact strength of the PBS/PBAT/miscanthus composites with a confidence level (α) of 0.05. According to the half normal probability plot the points which are farther away from the fitted line represent the significant effect on the impact strength. The points which appear close to the straight line indicate insignificant effects on the impact strength. In Fig. 3, it can be seen that all the significant factors (temperature and fiber length) are represented as square symbols while those not significant factors are presented as circle symbols.

The individual and interaction factors for the impact strength of the biocomposites can be investigated using a horizontal Pareto chart and the results are shown in Fig. 4. A Pareto chart is a bar chart that orders the bars from largest to smallest along with a vertical line. This chart is often used to analyze the statistical significant difference of the individual and interaction effects on the response. The vertical line in the Pareto chart indicates the significant factors on the response. For example, the bars extended to the right hand side of the vertical line are significant. In the present study, a Student's *t*-test was performed in a Pareto chart with 15 degrees of freedom at a 95% confidence interval. The *t*-value (vertical line in the chart) was found to be 2.57 which determine the significant factors and/or interactions on the impact strength of the composites. The fiber length (*D*) had significant effect upon the impact strength of the composites because the standardized effect value is higher than vertical line standardized effect value 2.57 (*t*-value). The processing temperature exhibited significant effect on the impact performance of the Mater-Bi®/miscanthus composites [6,13]. Contrary to our present result particle size did not significantly influenced the impact performance of the biopolymer/miscanthus composites [6,13]. This could be due to the morphological difference between the materials due to changing the processing variables.

Generally, the tensile toughness of the composites can be calculated from area under the stress–strain curve. Fig. 5 shows the stress–strain curves of PBS/PBAT composites with 2 mm miscanthus fibers (B) and 4 mm miscanthus fibers (A). These two composites are prepared with same processing conditions while changing fiber lengths. It can be noticed that the composites pre-

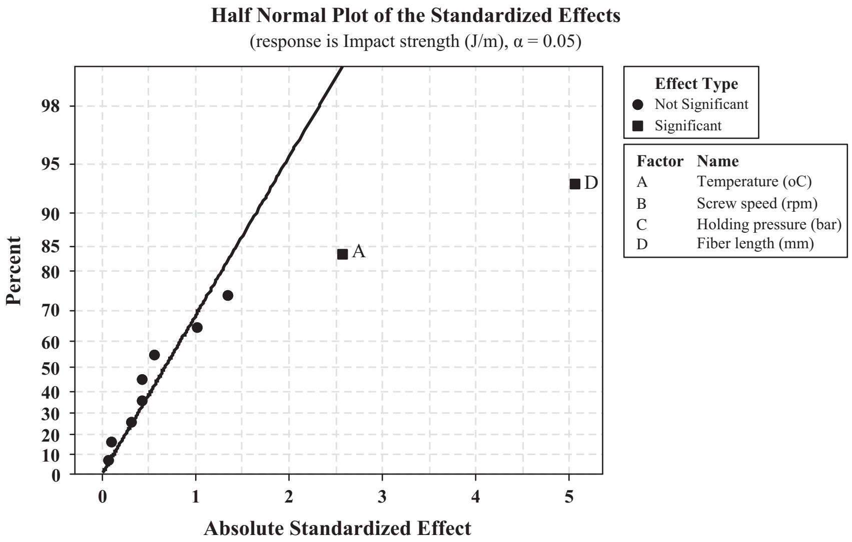

Fig. 3. Half normal probability plot of the standardized effects for impact strength of the PBS/PBAT/miscanthus biocomposites.

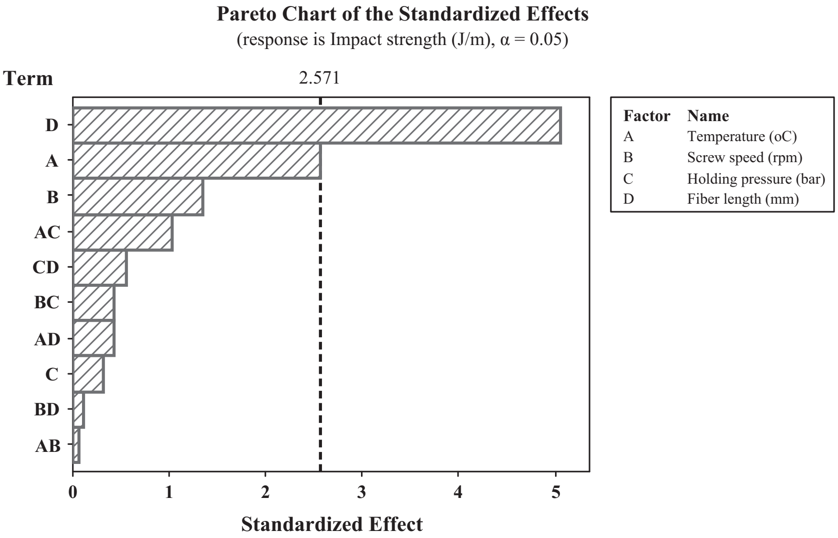

Fig. 4. Pareto chart of the standardized effects for the impact strength of the PBS/PBAT/miscanthus biocomposites.

pared with 2 mm fibers showed better tensile toughness compared to composites prepared with 4 mm fibers. This result has good agreement with observed impact strength of the composites with 2 mm fibers.

5.4. Fiber length distribution

Before and after processing, the length distribution of miscanthus fibers is shown in Fig. 6. After processing, the fiber length distribution is broader compared to before processing. At the same time, the fiber length is drastically reduced. It can be observed that the length of 4.65 and 2.07 mm miscanthus fibers is not significantly different after processing. For instance, after processing, the miscanthus fibers with average length reduced from 4.65 ± 2.5 to 1.07 ± 0.34 mm and from 2.07 ± 0.94 to 0.80 ± 0.39 mm. After processing, the length distribution of 4.65 mm fibers is varied from 0.45 to 1.9 mm while 2.07 mm fibers varied from 0.2 to 1.9 mm. This is because of the fiber breakage during extrusion in a twin screw extruder [22]. Moreover, the individualization of the fiber bundles during high mechanical shear produced in the compounding chamber is perhaps responsible for this observation. Similar trends were observed in the sisal fiber reinforced PBS composites [23] as well as kenaf fiber reinforced starch grafted PP composites [24]. The fiber length has a strong influence on mechanical performances [25]. It can be noted from Fig. 6, most of the fibers distributed with >0.9 mm length in the composites fabricated with 4.65 mm fibers. On the other hand, the composites processed with 2.07 mm fiber composites showed most of the fibers distributed <0.9 mm length in the resulting composites. Based on the fiber distribution after processing, more number of fiber ends can be observed in the composites prepared with 2.07 mm miscanthus fibers compared to 4.65 mm miscanthus fibers. Consequently, more number of fiber pull-outs can be expected from the composites prepared with 2.07 mm miscanthus fibers compared to 4.65 mm miscanthus fibers counterpart. The occurrence of more fiber pull-out may be responsible for the observed high impact strength in the composites prepared with 2.07 mm miscanthus fibers.

In general, the composites with a higher aspect ratio fiber should provide superior impact strength than the composites with

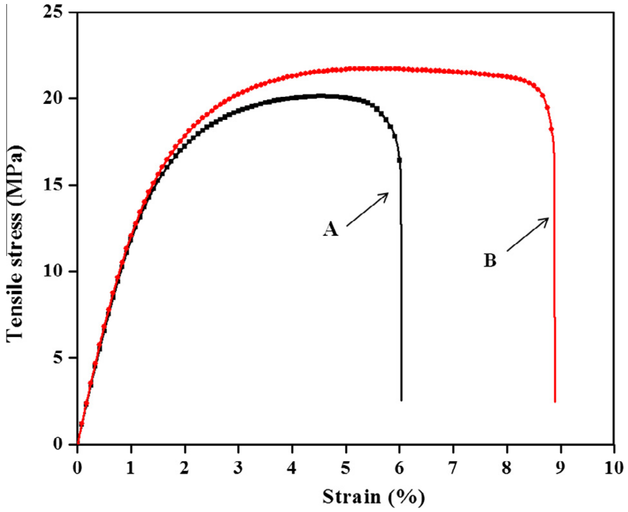

Fig. 5. Tensile stress–strain curves of PBS/PBAT/miscanthus composites with changing fiber length 4 mm (A) and 2 mm (B). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

lower aspect ratio fiber. For a given composites system, the recovered fiber length and aspect ratio were examined (Table 5) which revealed that the longer fibers had a higher aspect ratio (3.8) than short fibers (3.2) after processing. The composite with lower aspect ratio showed higher impact strength while the composite with higher aspect ratio had lower impact strength. This could be due to the difference in the fiber orientation during sample preparation [5,26,27]. The high aspect ratio fibers can align across the samples and thus fail to effectively transfer stress between the fiber and matrix. During impact fracture the crack initiation and propagation are mainly influenced by matrix behavior and morphology of the sample, respectively [28]. This phenomenon could play a vital role on the impact strength of PBS/PBAT/miscanthus composites when changing the fiber lengths.

5.5. Scanning electron microscopy

In order to study the impact fracture mechanism of PBS/PBAT/miscanthus composites, the surface morphology of the impact fractured samples was investigated by SEM analysis. The impact strength of the short fiber reinforced composites is influenced by many parameters including fiber pullout and degree of adhesion [29]. In the short fiber composites the fibers with subcritical aspect ratio lead to fiber pullout during fracture [30]. Fig. 7(a) and (b) represents the SEM morphology of the 2 mm miscanthus fiber reinforced PBS/PBAT composites and 4 mm miscanthus fiber reinforced PBS/PBAT composites, respectively. The SEM micrographs of both composites indicate that the fiber pullout mechanism and poor interfacial bonded regions played eminent role during impact fracture of the composites. There was no clear morphological

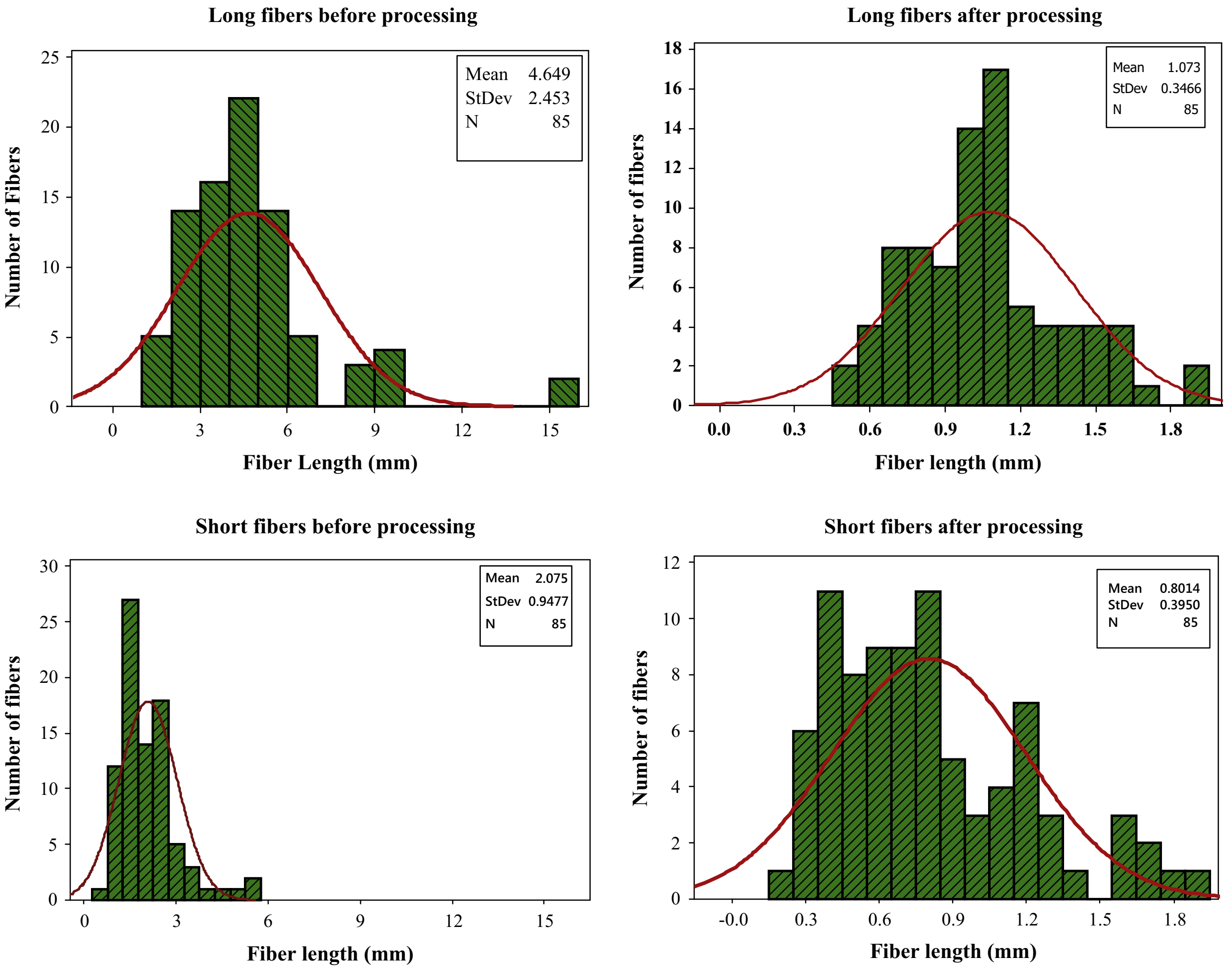

Fig. 6. Histograms of miscanthus fiber length distribution before and after compounding in a twin screw extruder. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 5
Average fiber length (*L*), average fiber diameter (*D*), and aspect ratio (*L*/*D*) of the miscanthus fiber before and after compounding.

Samples	Number of fibers	Average length (*L*) (mm)	Average diameter (*D*) (mm)	Aspect ratio (*L*/*D*)
Long fibers before compounding	85	4.65 ± 2.5	0.74 ± 0.024	6.3
Short fibers before compounding	85	2.07 ± 0.94	0.29 ± 0.13	7.13
Long fibers after compounding	85	1.07 ± 0.34	0.28 ± 0.11	3.8
Short fibers after compounding	85	0.80 ± 0.39	0.25 ± 0.09	3.2

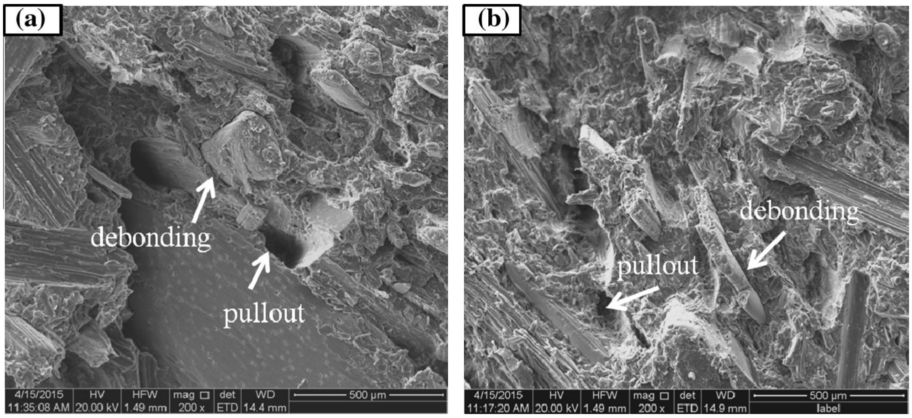

Fig. 7. Represents the SEM micrographs of the PBS/PBAT/miscanthus composites processed with 2 mm miscanthus fibers (a) and 4 mm miscanthus fibers (b).

difference witnessed in the composites with 2 and 4 mm fibers. However, the observed impact strength difference between the 2 mm fiber and 4 mm fiber composites may be due to the combined effects of pullout, energy dissipation mechanism and fiber orientation [30,31]. Further work could be performed to find out which mechanism is responsible to determine the impact strength of miscanthus fibers reinforced PBS/PBAT composites.

5.6. Mathematical model development

The predicated response of the composites is "*Y*" and it can be represented by Eq. (1) as a function of independent factors

$$Y = f(A, B, C, D) \tag{1}$$

The polynomial equation was used to explain the main and interaction effect of all the independent variables [15]. The polynomial equation can be expressed as follows,

$$\begin{aligned} Y = {} & X0 + X1(A) + X2(B) + X3(C) + X4(D) + X5(AB) + X6(AC) \\ & + X7(AD) + X8(BC) + X9(BD) + X10(CD) + X11(ABC) \\ & + X12(ABD) + X13(ACD) + X14(BCD) + X15(ABCD) \end{aligned} \tag{2}$$

The term $X0$ represents average response (impact strength) value, $X1$, $X2$, …, $X15$ is the regression coefficient of main and interaction effects, *A* is processing temperature, *B* is screw speed, *C* is holding pressure and *D* is fiber length. In Eq. (2), three and four factor interactions are not considered due to their insignificance [32]. Eq. (2) can thereby be modified as;

$$\begin{aligned} Y = {} & X0 + X1(A) + X2(B) + X3(C) + X4(D) + X5(AB) + X6(AC) \\ & + X7(AD) + X8(BC) + X9(BD) + X10(CD) \end{aligned} \tag{3}$$

The regression coefficients were calculated using MINITAB® 17 statistical software for impact strength. Substituting significant factors uncoded coefficient into Eq. (3), it can be rewritten as follows:

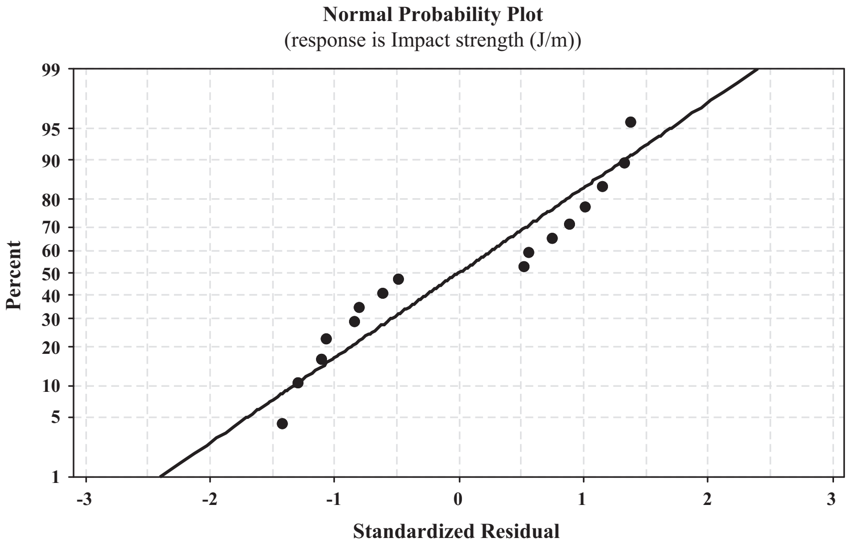

Fig. 8. Normal probability plot of the residuals for impact strength.

$$Y\ (\text{impact strength}) = 70.931 - 2.462\ (\text{temperature}) - 4.839\ (\text{fiber length}) \quad (4)$$

5.7. Diagnostic verification of the developed model

The assumption underlying the analysis of variance for each experimental design is similar to those required for a regression analysis. Assumptions for a completely randomized design are that the data for the treatment have normal probability distribution with equal variances. The assumptions can be checked with the residual plots. The normal probability plot/normal plot for the notched Izod impact strength of the biocomposites is shown in Fig. 8. To meet the normality assumption points should fall close to straight line on the normal plot. The normal plot of the impact strength data is dispersed along a straight line which indicates that the assumption of normal distribution is valid. The plot of residuals versus fit can be used to ensure the linear model adequacy. Fig. 9 shows the plot of the residual versus fit for impact strength of the PBS/PBAT/miscanthus composites. Fig. 9 shows the variation of impact strength from −1.5 to 1.5 J/m in between fitted and observed values. From the residual versus fit plot, the random scatter of residuals around the horizontal line can be seen which indicates that the model is adequate for impact strength data. The typical residual plot in Fig. 10 represents the residual versus observation order of the impact strength of PBS/PBAT/miscanthus composites. There is no distinct pattern observed in the residuals plot. Both positive and negative residuals are evenly distributed along theobservation order in Fig. 10. This observation suggests that the impact strength of PBS/PBAT/miscanthus composites is distributed normally.

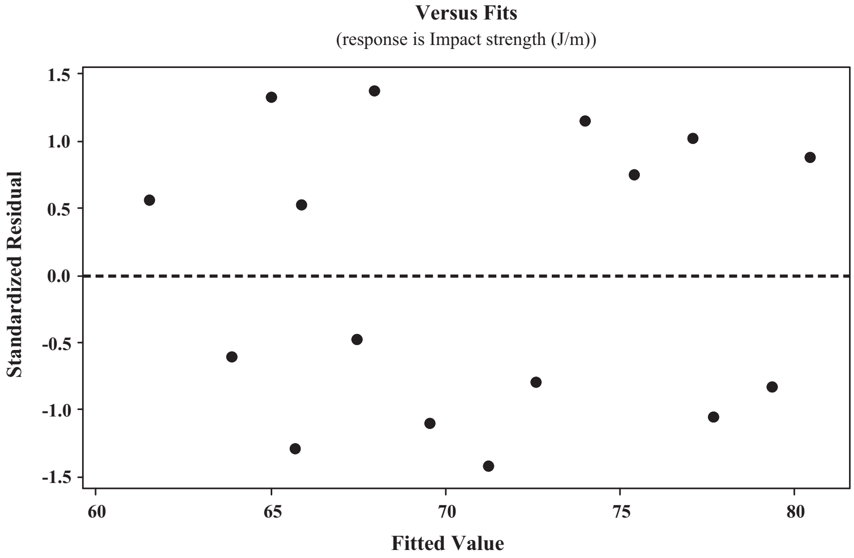

Fig. 9. Residual plots versus fitted values for impact strength.

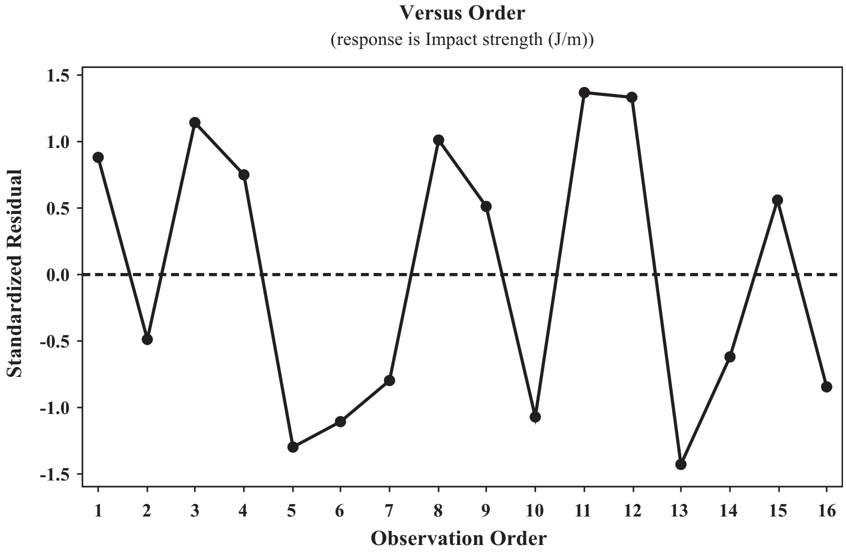

Fig. 10. Variation of the residuals versus observed order values of the impact strength.

6. Conclusions

In conclusion the miscanthus fibers can be used as a reinforcing agent for tough biodegradable polymers. The stiffness and flexural strength of the PBS/PBAT (60/40 wt%) blends is improved with addition of miscanthus fibers. This is a common observation in natural fiber reinforced composites. The impact strength of the PBS/PBAT blend was considerably reduced after incorporation of miscanthus fiber into PBS/PBAT blend matrix. This could be due to the phase separation of the components in the multiphase material. However, the composites with 2 mm fiber showed superior impact resistance than 4 mm fiber reinforced composites. This impact strength variation could be due to the difference in fiber pull-out mechanism during impact test. The influence of independent processing variables on the impact strength of PBS/PBAT/miscanthus composites has been investigated by 2^4 full factorial design of experiment. Using student's *t*-test and *F*-test, the statistically significant main and interaction variables were analyzed at a 95% confidence level. According to main effect plot, Pareto plot, and half normal plot, the fiber length plays an important role on the impact strength of the composites as does processing temperature. From the normality plot it was observed that the data are normally distributed along the straight line with R^2 value of 87.78%. Further work could be performed by maximizing more number of variables as well as levels.

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