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Application of response surface methodology (RSM) in analyzing the hydrolytic degradation of plasticized MWCNTs nanocomposites

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Abstract. The present research goals are to investigate how several parameters became the factor to maximize the degradation ability of biopolymer. Multi-walled carbon nanotubes (MWCNTs) was blended in poly(lactic acid (PLA) assisted by poly(ethylene glycol) (PEG) as a plasticizer. PLA/PEG/mCNTs from the melt blending technique was used for analysis in hydrolysis degradation purposely to discover how the time, temperature and pH of media solution could affect the weight loss and validate by Response Surface Methodology (RSM). The hydrolysis study was examined at three parameters of immersion; time from 7 to 28 days; the temperature at 25 ^{o}C, 45 ^{o}C and 65 ^{o}C; and pH of the solution at pH 3 (HCl), pH 6.5 (deionized water) and pH 10 (NaOH). The maximum weight loss, 22.53 % was observed after 28 days of immersion at 65 ^{o}C of immersion temperature and pH 3 of solution. The quadratic model developed was reasonably accurate based on the R^2 value of 0.966, insignificant lack of fit, and low percentage error during validation experiment from the predicted values (< 5 %).

Keywords: Poly(lactic acid), carbon nanotubes, melt blending, degradation behaviour

1. Introduction

Plastics are low-cost, lightweight, and long-lasting materials that may be easily moulded into a variety of objects for a wide range of purposes. As a result, over the previous 60 years, the output of plastics has expanded dramatically. Current levels of consumption and disposal, on the other hand, result in a plethora of environmental difficulties. As a result, there has been a recent spike in interest in developing alternative and biodegradable polymers derived from renewable resources. PLA is a biodegradable polymer that has been investigated for a range of applications in engineering fields such as automotive, aerospace, and aeronautics, as well as in the biomedical field, with the goal of boosting component autonomy and efficiency. When it comes to processing properties, it's worth noting that adding plasticizer to highly loaded PLA can help with filler dispersion and viscosity control. A study [1] showed how plasticized PLA was made using poly(ethylene glycol) (PEG) and melt mixing. The addition of 4.0 wt.% MWCNTs increased the dielectric characteristics and shielding efficiency. Furthermore, because the plain PLA has a low tendency to degrade,

the PEG helps to boost the biodegradation rate [2]. Furthermore, because the neat PLA has a low tendency to deteriorate, the PEG aids in increasing the biodegradation rate.

The inclusion of nanoparticles in the polymer can cause the ester bonds on the polymer's main chain to cleave more quickly due to an increase in the amount of water in the matrix. PLA experiences major physical changes when exposed to water: it plasticizes and expands, its glass transition temperature and mobility drop, and crystallisation kinetics speed up [3,4]. Hydrolysis reduces the molecular weight over a longer duration, influencing the physical and mechanical properties. The hydrolytic degradation, in particular, has been extensively researched, and the fundamental elements influencing this phenomena are well understood. The use of laboratory-scale experiments to explore biodegradability and biodegradation mechanisms of biodegradable materials is an incredibly significant technique for evaluating the service life of these materials from both an industrial and scientific standpoint. A two-step technique is the most widely accepted approach for PLA biodegradation [5]. Heat and moisture in the compost break down the PLA chains at first, resulting in lower molecular weight polymers and, eventually, lactic acid. Microorganisms in the compost and soil then mineralize the oligomer fragments and lactic acid to produce methane and carbon dioxide under both anaerobic and aerobic conditions.

Surprisingly, when temperatures around the T_g of PLA are explored, the impacts of water are typically measured at times when the hydrolysis has already caused considerable changes in the material, such as after a few days or weeks [6,7]. This makes it hard to control to what extent other inside-the-material phenomena like opacification and crystallinity evolution can evolve independently. This makes it difficult to determine to what extent other inside-the-material phenomena like opacification and crystallinity evolution can evolve independently. This makes it difficult to determine to what extent other inside-the-material phenomena like opacification and crystallinity evolution can evolve independently.

In current study, a biodegradable polyester, poly(lactic acid) (PLA) as a matrix has been chosen to be modified with carbon-based materials. The main target was to study the modelling and optimization of the operating parameters such as temperature, time and pH on the weight loss of MWCNTs.

2. Materials and methods

This RSM analysis is a continuation of a previous study [7]. In the study, the maximum hardness and melt flow index (MFI) was obtained from PLA/PEG with 1.5 wt.% of mCNTs the melt blending method. The sample was cut into 10 mm squares to examine the elements that influence the maximum weight loss. To achieve the consistent weight, the samples were dried at 60°C. The samples were then immersed in a 50 ml beaker containing 30 ml distilled water and kept in the laboratory for up to 28 days with varied pH media at room temperature (25 oC), 45 oC, and 65 oC. Hydrochloric acid, HCl (pH 3), deionized water, DI (pH 6.5), and sodium hydroxide, NaOH were utilised as media solutions (pH 10). The weight loss of the samples was measured on a regular basis by removing them from the water bath for a length of time and drying them in a 60 oC oven to eliminate moisture. The samples were then weighed, and the weight loss was recorded using the equation (1). The samples were returned to the water bath and the process was repeated until the samples had been immersed for 28 days.

$$\Delta W_{loss} = [(W_i - W_f)/ W_i] \times 100 \tag{1}$$

3. Results and discussion

3.1 Determine the Effect of Solution Immersion Parameters on PLA Nanocomposite using RSM

Polymer nanocomposite with mCNTs nanofiller has the potential to be used as sensing, flexible electronics and tissue engineering scaffold applications. It means during the application, these materials must have excellence in mechanical and thermal properties, but at the same time, they must be able to degrade after some time. Furthermore, the purpose of tissue engineering is to allow the body's cells to progressively replace the scaffold that has been implanted. As a result, the scaffolds must be biodegradable, with the degradation products being non-toxic and able to exit the body without harming other organs. [8,9]. As a result, the importance of the current study could be underlined as to why weight loss in solution immersion occurs.

Even we need nanocomposites with a high degradation rate; we need to consider the properties due to their application during their lifetime. The main purpose is to determine which parameter mostly affects weight

loss. The solution immersion involved the hydrolysis reaction that brought to chain scission, measured by weight loss of nanocomposite. The hydrolysis reaction is autocatalytic, according to several studies [10,11], and the rate of reaction is improved by increasing the carboxylic end group concentration. The rate of hydrolysis should be proportional to the concentration of carboxylic end groups when this mechanism is examined. The general hydrolysis reaction that takes place within the samples can be expressed as in equation (2).

$$H_2O + ester \leftrightarrow -COOH + -OH \qquad (2)$$

The hydrolysis produced by water transport is the fundamental driving force behind PLA degradation [12]. This motivates the rational design of usage-adaptive degrading features, which is both economically and intellectually appealing for the expansion of PLA's applications [13–14].

The RSM based on Central Composite Design (CCD) was used to evaluate the consequence of independent variables; temperature, time and pH on the weight loss as the response function. A three-factor three-level response surface CCD was selected in this study to achieve the objective. The significance of the independent variables and their interactions was run by using an analysis of variance (ANOVA). The variables and experimental ranges are presented in table 1.

Table 1. Experimental design for optimisation of weight loss

Run	Variables			Actual response
	Temperature (^{o}C)	Time (Day)	pH	Weight loss (%)
1	45	17.5	3.0	14.760
2	65	28.0	10.0	20.546
3	45	17.5	6.5	5.003
4	25	17.5	6.5	2.232
5	45	28.0	6.5	5.034
6	25	28.0	10.0	6.544
7	45	17.5	6.5	4.880
8	25	7.0	3.0	5.276
9	65	7.0	10.0	6.298
10	65	28.0	3.0	23.432
11	25	28.0	3.0	7.987
12	45	17.5	6.5	5.235
13	45	17.5	6.5	5.630
14	45	7.0	6.5	1.945
15	65	17.5	6.5	5.413
16	45	17.5	6.5	4.938
17	45	17.5	6.5	2.690
18	45	17.5	10.0	10.632
19	65	7.0	3.0	8.423
20	25	7.0	10.0	4.235

Basically, during solution immersion, the tortuous pathway for H_2O molecules to diffuse inside the nanocomposite when using a nanofiller was created. Thus, the solution absorbency of PLA/PEG/mCNTs nanocomposite was affected by functional groups devoted to the surface of CNTs. Besides, these three parameters were the co-factors that contributed to the solution immersion which resulted in the weight loss of nanocomposite. The general quadratic model for the three factors obtained can be expressed in equation (3).

$$Y = X_0 + X_1A + X_2B + X_3C + X1_1A^2 + X_{22}B^2 + X_{33}C^2 + X_{12}AB + X_{13}AC + X_{23}BC \qquad (3)$$

Analysis of variance (ANOVA) was applied to assess the quality of the developed model. A polynomial equation showed the influence of experimental variables on weight loss. The quadratic function in terms of actual factors is given in equation (4).

$$Weight\ loss = + 20.36 + 0.19(temperature) + 0.15(time) - 8.43(pH) - 2.46 \times 10^{-3}(temperature)^2 - 0.01(time)^2 + 0.64(pH)^2 + 0.01(temperature \times time) - 4.51 \times 10^{-3}(temperature \times pH) - 3.96 \times 10^{-3}(time \times pH) \tag{4}$$

The significance of the model was evaluated from the value of coefficients of determination, normal probability plot and residual analysis. As presented in table 2, the coefficients of determination (R^2) are 0.9497 while the adjusted R^2 value is 0.9045. There is no significant difference between R^2 and adjusted R^2 as the difference in value is less than 0.2. This means that 94.97 % of the total variation in weight loss is in great agreement with the experimental variable studies. In addition, a small value of standard deviation (1.77) and R^2 value close to unity indicates that the predicted value can resemble the actual response value. Adequate precision greater than 4 indicates an adequate signal.

Table 2. ANOVA analysis for response surface model of weight loss.

Source	Sum of squares	Degree of freedom	Mean square	F value	P-value Prob > F	
Model	594.53	9	66.06	20.99	<0.0001	significant
A-Temperature	143.17	1	143.17	45.49	<0.0001	significant
B-Time	139.62	1	139.62	44.36	<0.0001	significant
C-pH	13.51	1	13.51	4.29	0.0651	
A^2	2.65	1	2.65	0.84	0.3803	
B^2	4.76	1	4.76	1.51	0.2471	
C^2	171.26	1	171.26	54.41	<0.0001	significant
AB	73.43	1	73.43	23.33	0.0007	significant
AC	0.80	1	0.80	0.25	0.6255	
BC	0.17	1	0.17	0.054	0.8214	
Residual	31.47	10	3.15			
Lack of Fit	26.11	5	5.22	4.86	0.0537 not significant	
Pure error	5.37	5	1.07			
Cor. Total	626.01	19				
Standard Deviation	1.77		R^2		0.9497	
Mean	7.56		Adjusted R^2		0.9045	
C.V.	23.48		Pred. R^2		0.6650	
PRESS	209.74		Adeq. Precision		18.181	

The significance of each term and variable was determined by their F-value and P-value. A large F-value with a P-value of less than 0.05 indicates that a 95 % confidence level of that particular term affected the weight loss of PLA/PEG/mCNTs nanocomposite. On the contrary, P-value larger than 0.05 is considered to have no statistical effect on the response model. The F-value for this model is 20.99 and the P-value is 0.0001 which is a suggestion that the model is significant. Furthermore, factors A, B, C^2 and AB are the significant factors that gave the largest effects on weight loss. All of the other terms had less than 95% confidence level indicating that their effect is not significant. The lack of fit in this model is not significant ensuring that the model fits well with the experimental data. The lack of fit test is crucial to ensure that the replicated error in comparison to the model-dependent error is not significant [14].

3.2 Analysis of weight loss factors by 3D-curves

The figures below illustrate the effect of different factors on weight loss by using 3D curves. Figure 1 shows the interaction between temperature and time to weight loss of PLA/PEG/mCNTs nanocomposites. The

weight loss increases proportionally upon longer immersion time up to 28 days and maximum temperature at 65 ^{o}C. It supports that, at 1.5 wt.% of mCNTs loading, longer immersion time and higher temperature increase the weight loss to the maximum. This has been postulated that thermal degradation mainly occurs by main-chain scission [15]. When studying temperatures near the glass transition of PLA, it's worth noting that the impacts of water are usually observed after the hydrolysis has already caused major changes in the material, such as after a few days or weeks [16]. With the progression of degeneration, the two causes became apparent. The number of carboxylic acid chain ends known to autocatalyze ester hydrolysis grows as the matrix degrades, and only soluble oligomers in the surrounding aqueous media escape from the matrix [17].

Furthermore, increasing the immersion temperature improved both the diffusion coefficient and the maximum moisture content for a given mCNTs content. The activity of the water molecule, which was impacted by temperature, controlled water diffusion in nanocomposite. As a result, the increased activity of the water molecules at 65 ^{o}C can be linked to the rapid rise in weight loss compared to 25 ^{o}C. As a result, it is clear that reaching equilibrium moisture content values at 25 ^{o}C takes substantially longer than at 65 ^{o}C. The same findings were reported by several kinds of researches whereby increasing immersion temperature and immersion time, the water sorption increased [18,19].

Temperature plays a crucial role in the hydrolysis degree of degradation of PLA increases with temperature, resulting in faster cleavage of the ester bonds. Nevertheless, PLA was susceptible to thermal degradation during the process, leading to a decrease in M_w and the rheological and mechanical properties of processed PLA parts. PLA thermal degradation is influenced by the hydrolysis induced by remaining water during processing, the unzipping depolymerization reaction, random main-chain scission, and intramolecular and intermolecular transesterification. As a result, drying PLA resins before processing is strongly recommended. The temperature, 65 ^{o}C was selected as the maximum point in the range because at the elevated (58–60 ^{o}C) or above the T_g of PLA, the M_w will be reduced, followed by the biodegradation process.
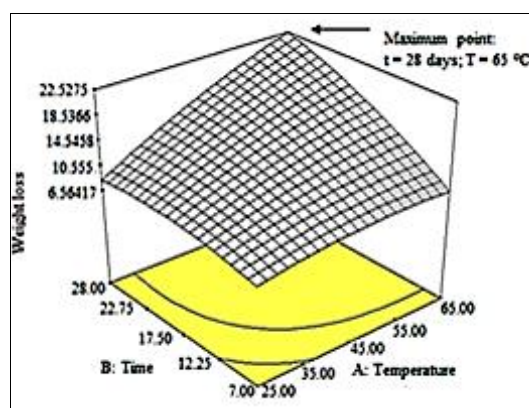

Figure 1. The effect of immersion temperature and time on weight loss

Figure 2 shows the effect of immersion temperature and pH on a weight loss of nanocomposite. It reveals the weight loss decreases when solution pH ranges between 4.75 to 8.25 and immersion temperature at 25 ^{o}C. At maximum temperature (65 ^{o}C), the weight loss starts to increase from the neutral solution (pH 6.5) to the basic solution (pH 10), whereas maximum weight loss is reported in acidic solution at pH 3. It can be seen; the combined factors of high temperature and acidic conditions influence the weight loss rate to the maximum in this study. An acidic environment will catalyse the deterioration of tissue engineering devices such as implants, causing a further fall in pH and perhaps causing undesirable tissue reactions [20]. Depending on the nature of the medium, two primary mechanisms have been reported in the case of PLA [9]. In acidic environments, protons catalyse the hydrolysis of ester bonds, particularly the cleavage at terminal esters. The hydrolysis of ester bonds catalysed by protons is prominent in acidic conditions, particularly the cleavage at terminal esters. Lactide and the cyclic dimer of lactic acid were formed in basic environments as a result of a preferential backbiting process.
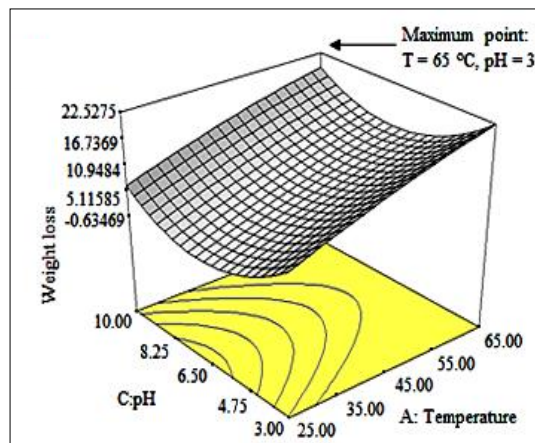
Figure 2. The effect of immersion temperature and pH on weight loss.

Figure 3 illustrates the effect of interaction between immersion time and solution pH on the weight loss of nanocomposite. The weight loss reaches the maximum rate at pH 3 after 28 days of immersion. The minimum weight loss is observed at pH 6.5 in deionized water after 7 days of immersion, which is similar to a report by other research [21]. It means, without co-factor such as acidic and basic medium and high thermal conditions, the degradation rate of nanocomposite gives the smallest value in the neutral condition. The one-dimensional Fick's second rule, which states that moisture rises with time, is often found to govern the kinetics of water diffusion in a sheet of polymer [22].
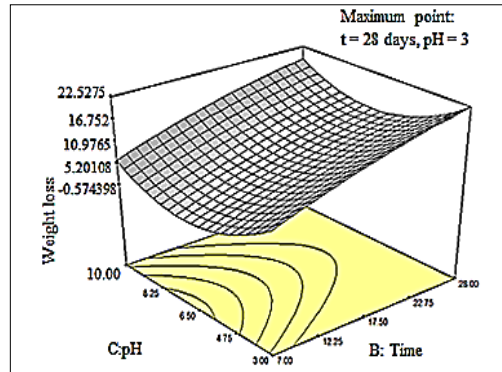

Figure 3. The weight loss effect of immersion time and pH.

PLA containers, as an example of applications, have been designed to interact with water, cold-chain dairy, and juices, allowing the PLA to interact with a variety of settings with varying pH and polarity. The rate of hydrolysis of PLA-based polymers is influenced by the medium pH. Polymer chains are more easily destroyed in strong basic and acidic conditions because hydrolysis reactions are facilitated by the presence of hydronium and hydroxide ions [23]. If PLA is used to make a citrus juice bottle, it will be subjected to acidic media (pH 4), causing the hydrolysis mechanism to continue through chain-end scission.

The simulation points from Design Expert in the optimization process are shown in table 3. Only one solution is suggested for the optimum response which is 65.00 $^{\circ}$C of temperature in 28.00 days of immersion at pH 3. The actual experiment was done as suggested. The desirability value of 0.904 indicates that this recommendation is suitable to be used. The experiment was performed three times for validation purposes.

Table 4 shows the results of the validation experiment conducted at an optimum combination. It is observed that the errors of experimental values and predicted values for weight loss are less than 5%. The

experimental data are within 95% of the suggested prediction tolerance from the predicted values which indicates that the experiment is replicable. It can also be confirmed that the model equation is reasonably accurate.

Table 3. Recommend optimum parameters for maximum weight loss of the PLA/PEG/mCNTs nanocomposite.

Number	Temperature (^{o}C)	Time (day)	pH	Weight loss (%)	Desirability
1	65.00	28	3.00	22.528	0.904

Table 4. Results of validation experiment shown at an optimum parameters.

Run no.	Temperature	Time (day)	pH	Weight loss		
				Predicted	Experimental	Error (%)
1	65.00	28.00	3.00	22.53	23.40	3.86
2	65.00	28.00	3.00	22.53	21.95	2.57
3	65.00	28.00	3.00	22.53	23.42	3.95

4. Conclusion

Design-Expert software was used in the validation of weight loss, the effect of immersion condition and their interaction can be investigated. Three factors of processing parameters were studied which were immersion temperature, time and pH. The observation revealed that all three factors had a noteworthy influence on the weight loss of PLA/PEG/mCNTs. The optimum condition was reported at 65 ^{o}C of immersion temperature in 28 days of immersion at pH 3 with a weight loss of 22.53 %. The quadratic model developed was reasonably accurate based on the R^2 value of 0.966, insignificant lack of fit, and low percentage error during validation experiment from the predicted values (< 5 %). Thereby, this model is considered acceptable to be used in future applications.

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