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Gum colocasia-g-polyacrylamide: Microwave-assisted synthesis and characterization

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ABSTRACT

In the present investigation, an attempt has been made for grafting of acrylamide on the backbone of Colocasia esculenta by using microwave-assisted grafting method, which is a convenient and versatile route for the development of polysaccharide-based materials. The dried mucilage of colocasia was prepared from fresh rhizomes. The optimization was performed by using Box Behnken matrix design (BBD) and response surface methodology (RSM) using design expert software. A series of graft polymers, varying in the amount of acrylamide, ammonium persulphate and microwave irradiation was prepared. The effect of Microwave time, gum concentration and power on percentage yield, percentage grafting and percentage grafting efficiency has been optimized and evaluated by 3D surface response graphs. It has been observed that power and irradiation time has a significant synergistic effect on % yield, % grafting and % grafting efficiency however gum concentration produce slight increment up to a limit after that the effect becomes almost constant. The selected optimized formulation is F_8 with a percentage yield of 99.57%, percentage grafting of 634.33% and percentage grafting efficiency of 87.49%. Optimized formulation was subjected to Fourier transform infrared spectroscopy, Differential scanning calorimetry, X-ray diffraction and Scanning electron microscopy for characterization which committed the grafting of acrylamide on Colocasia esculenta.

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INTRODUCTION

Natural gums and their derived products are the polymeric materials which are widely used in pharmaceutical products. These polysaccharides are biodegradable and used in the release of freely soluble drugs at a constant rate (Bhardwaj *et al.*, 2000). The natural gums have been used in the preparation of matrix for preparation of sustained-release formulations. In water, the natural gums will create a gel-like structure, and the drug will produce a prolonged effect after release (Setia and Kumar, 2014). Natural gums have certain advantages over synthetic materials like low price, biodegradability, nontoxic and ease of availability. However, natural gums have certain disadvantages like unconfined hydration, viscosity reduction and highly prone to microbes, to overcome these drawbacks, natural gums are modified by using various approaches (Parmar *et al.*, 1997).

Grafting of polymeric chains is one of the best approaches for modification of natural gums. In this process, a copolymer is produced by binding of monomers on the backbone of a polymeric chain which can be used in the formulation of controlled drug delivery systems (Vijan *et al.*, 2012; Mehr and Kabiri, 2008).

In this investigation, a grafted copolymer of Colocasia Esculenta and acrylamide was synthesized and optimized.

Colocasia esculenta belongs to the Araceae family. This plant is a monocot, mainly tubers and leaves of the plant are used. The corms contain significantly less amount of lipids, vitamins and proteins, but contains a high amount of carbohydrates. The crude taro gum has been investigated as binding and emulsifying agents (Sanful, 2011; Njintang *et al.*, 2014). Colocasia contains 70 to 80 % starch (Kaur *et al.*, 2013).

MATERIALS AND METHODS

Colocasia Esculenta was procured from the domestic market. Ammonium persulfate and acrylamide were purchased from LOBA Chemicals. All analytical grade chemicals were used.

Extraction of Colocasia esculenta Mucilage

The fresh rhizomes of colocasia were crushed after washing. Boiling for half an hour was given after soaking of 20 g of tubers in 200 ml of water. After boiling the mixture is allowed to stand for one hour as such for a complete release.

Muslin bag was then used to separate mucilage from marc. Mucilage was then precipitated by addition of acetone. After separation of mucilage, the drying was done at 40^{o}C. The dried mucilage was then passed through # 80 sieve and then preserved into a desiccator (Alalor *et al.*, 2014).

Grafting of extracted mucilage

Grafting of extracted mucilage with acrylamide was done by employing microwave-assisted grafting. The distilled water was used to dissolve an appropriate amount of mucilage by stirring for one h. Acrylamide was dissolved in the above mixture using stirring.

For grafting, ammonium persulphate as initiator was added to this above solution and irradiated to microwave (NN-CT654M, Panasonic Japan) at different power and time. After that, acetone (3 times in volume) was added and kept overnight to allow the formation of precipitates.

The final solution was filtered using Whatman filter paper, and the precipitate was washed with water: methanol (20:80) to remove unreacted monomer and initiator.

The drying of the final mucilage was performed at 40^{o}C for 24 h (Kumar *et al.*, 2009; Ghosh *et al.*, 2010).

Experimental Design

The optimization was performed by using Box Behnken design. The three levels are required for this design which was coded as -1,0 and 1.

The design expert software (version 7.0) was used for optimization with 3 dependent and 3 independent variables.

The percentages of Gum concentration (X1), Power (X2) and Irradiation time (X3) were selected as independent variables while % Yield (Y1), % Grafting (Y2) and % Grafting efficiency (Y3) were selected as dependent variables as shown in Table 1.

The nonlinear quadratic model by this design is given as

$$Y = \beta_0 - \beta_1.X_1 + \beta_2.X_2 + \beta_3 X_3 - \beta_4.X_1.X_2 - .X_1.X_3 - \beta_6.X_2.X_3. - X_1^2 - \beta_8.X_2^2 + \beta_9.X_3^2$$

Where Y is the response of the dependent variable, an intercept is designated as β_0, and the regression coefficients are designated as β_1– β_9 obtained from the observed experimental values of Y.

Values of the independent variables are coded as X_1, X_2 and X_3. X_1 X_2 X_3 (a, b = 1, 2, 3) and X^2i (i = 1, 2, 3) represent the interaction and quadratic terms, respectively (Abbas *et al.*, 2017).

The characterization of grafted colocasia copolymer was performed by DSC (Differential Scanning Calorimetry), FTIR spectroscopy (Fourier transform infrared spectroscopy), XRD (X-ray Diffractometry) and SEM (Scanning electron microscopy).

Further, the grafted copolymer was subjected to % grafting (%G), % grafting efficiency (%GE) and % conversions by using the following formulae (Nandi *et al.*, 2019):

$$\%\ \text{Grafting}\ (\%G) = \left(\frac{W_1 - W_0}{W_0}\right) * 100$$

$$\%\ Grafting\ Efficiency\ (\%GE) = \left(\frac{W_1 - W_0}{W_2}\right) * 100$$

$$\%\ Conversion\ (\%C) = \left(\frac{W_1}{W_2}\right) * 100$$

Where W_0 is the weight of original Colocasia, W_1 is the weight of grafted colocasia and W_2 denote the weight of monomer used.

Fourier Transform Infrared Spectroscopy

The ungrafted and grafted copolymer was subjected to Fourier transform infrared spectroscopy by

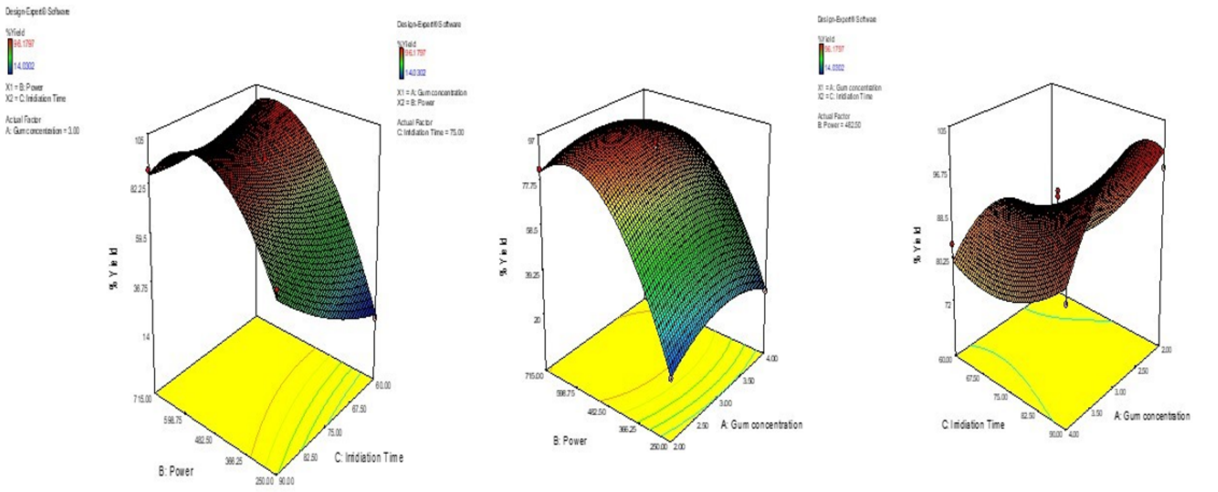

Figure 1: a) 3D surface response graph between Power (X2), irradiation time (X3) and % yield (Y1); b) 3D surface response graph between Gum concentration (X1), power (X2) and % yield (Y1); c) 3D surface response graph between Gum concentration (X1), irradiation time (X3) and % yield (Y1)

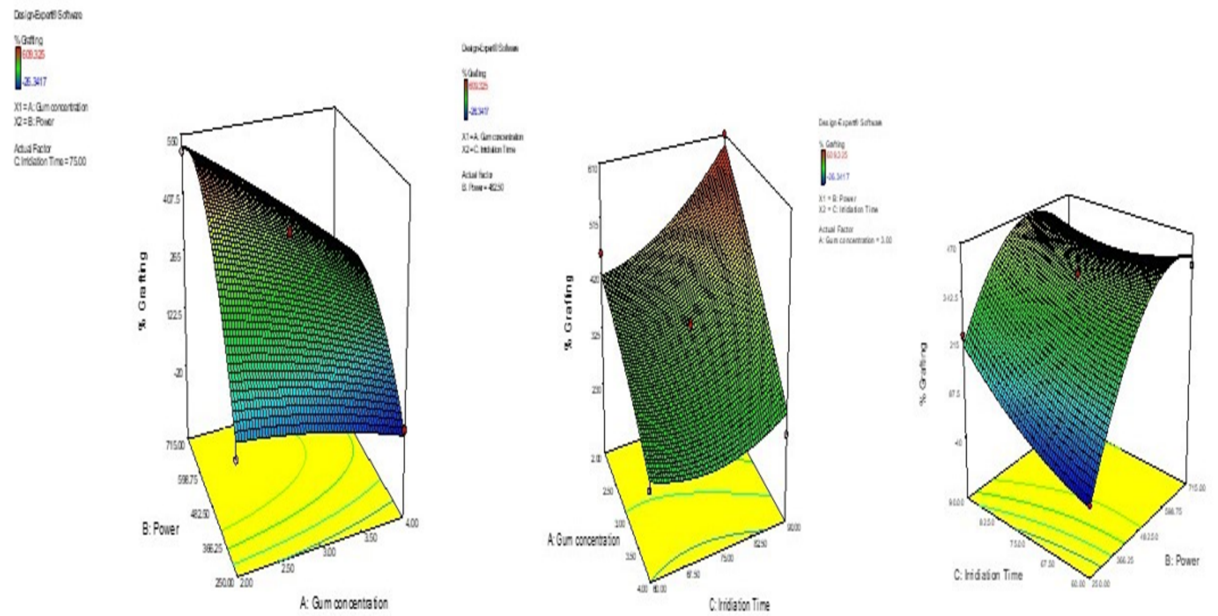

Figure 2: a) 3D surface response graph between Gum concentration (X1), power (X2) and % grafting (Y2); b) 3D surface response graph between Gum concentration (X1), irradiation (X3) and % grafting (Y2); c) 3D surface response graph between Power (X2), irradiation time (X3) and % grafting (Y2)

Table 1: Box Behnken Design containing levels of variables

Factor	Name	Unit	Min. (-1)	Mid-level (0)	Max. (+1)	Responses Taken	Name	Units
X1	Gum concentration	%	2	3	4	Y1	%Yield	%
X2	Power	Watt	250	440	715	Y2	% Grafting	%
X3	Irradiation time	seconds	60	75	90	Y3	%Grafting efficiency	%

Table 2: Box-Behnken Design Matrix

Formulation code	Gum conc. (gm) X1	Gum conc. (%)	Power (W) X2	Irridiation time (sec) X3	Acrylamide amount (gm)	APS (mg)
F1	0.8	2	250 (P-30)	75	5	0.1
F2	1.2	3	440 (P-50)	75	5	0.1
F3	1.2	3	440	75	5	0.1
F4	1.2	3	250	90	5	0.1
F5	0.8	2	440	60	5	0.1
F6	1.6	4	250	75	5	0.1
F7	1.2	3	440	75	5	0.1
F8	0.8	2	440	90	5	0.1
F9	1.6	4	440	60	5	0.1
F10	1.2	3	715 (P-80)	90	5	0.1
F11	1.2	3	715	60	5	0.1
F12	1.2	3	440	75	5	0.1
F13	1.2	3	250	60	5	0.1
F14	1.2	3	440	75	5	0.1
F15	1.6	4	715	75	5	0.1
F16	0.8	2	715	75	5	0.1
F17	1.6	4	440	90	5	0.1

using KBr pellet in Fourier Transform Infrared spectrophotometer (Vijan *et al.*, 2012).

Differential Scanning Calorimetry

The samples of Colocasia esculenta and Grafted Colocasia esculenta were subjected to Differential Scanning Calorimetry in the temperature range of 40^{0}C -250^{0}C (Kaity *et al.*, 2013).

XRD analysis

X-ray diffractogram of pure drug and excipients was recorded by employing Ultima-4, Rigaku company, Japan) using K-beta filter (Singh *et al.*, 2011).

Scanning Electron Microscopy

Colocasia esculenta and grafted colocasia esculenta particles were subjected to Scanning electron microscopy (Model: JSM 5200, Japan). Samples were exposed to vacuum for 5-10 min. At 40 mA and investigated at accelerating voltage of 15 kV and 10 kV (Mahto *et al.*, 2014).

RESULTS AND DISCUSSION

Preparation and Optimization of Colocasia-g-poly(acrylamide)

The extracted and dried mucilage of Colocasia esculenta was used for graft copolymerization using microwave-assisted grafting. Researchers are more attracted to this method, as this method is superior to conventional grafting methods. Gum Aegle marmilos (Setia and Kumar, 2014), gum ghatti (Rani *et al.*, 2012) and gum agar (Mishra *et al.*, 2011) have been grafted successfully by the researchers. The proposed mechanism for grafting of acrylamide on the surface of gum is given below:

$$CO6H + A \xrightarrow{MW} CO^{*} + A^{*}$$

$$CO^{*} + A \rightarrow COA^{*}$$

Table 3: Box-Behnken Design Matrix

Formulation code	Yield	% Yield (Y1)	% Grafting (Y2)	% Grafting efficiency (Y3)	% conversion
F1	1.2155	20.60	51.94	7.16	24.31
F2	5.758	91.40	379.83	73.52	115.16
F3	5.511	87.48	359.25	69.53	110.22
F4	4.009	63.63	234.08	45.31	80.18
F5	4.4618	75.62	457.73	63.13	89.24
F6	1.5758	23.52	-1.51	-0.37	31.52
F7	5.827	92.49	385.58	74.63	116.54
F8	5.8746	99.57	634.33	87.49	117.49
F9	5.5631	83.03	247.69	60.05	111.26
F10	5.6025	88.93	366.88	71.01	112.05
F11	5.8729	93.22	389.41	75.37	117.46
F12	5.593	88.78	366.08	70.85	111.86
F13	0.8839	14.03	-26.34	-5.10	17.68
F14	5.59	88.73	365.83	70.81	111.80
F15	4.892	73.01	205.75	49.88	97.84
F16	4.8838	82.78	510.48	70.41	97.68
F17	5.5868	83.39	249.18	60.41	111.74

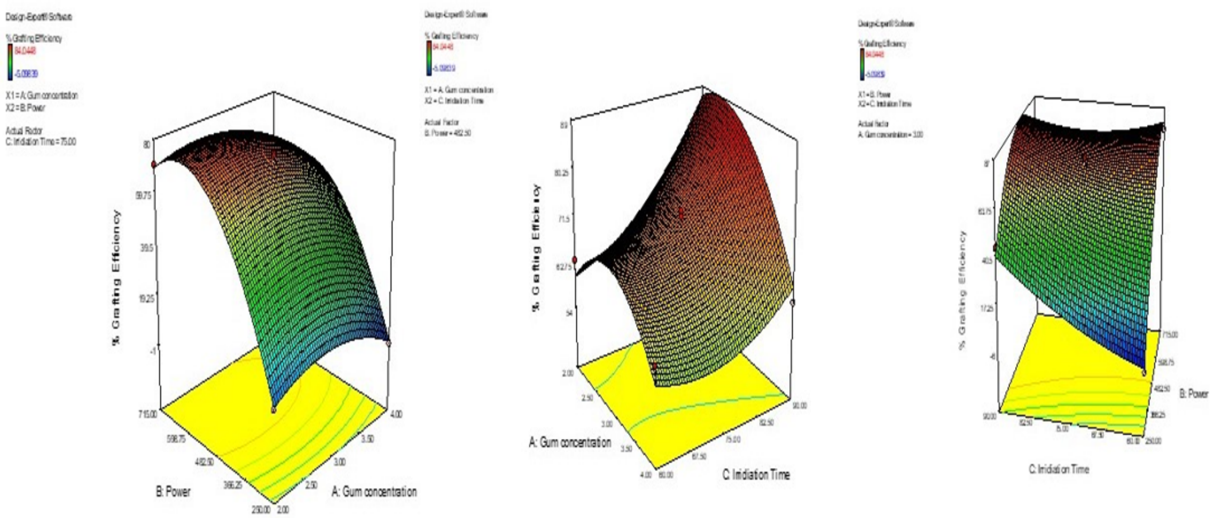

Figure 3: a) 3D surface response graph between Gum concentration (X1), power (X2) and % grafting efficiency (Y3); b) 3D surface response graph between Gum concentration (X1), irradiation (X3) and % grafting efficiency (Y3); c) 3D surface response graph between Power (X2), irradiation time (X3) and % grafting efficiency (Y3)

$$COA^{*} + A \rightarrow COAA^{*}$$
$$COAA_{n-1} + A \rightarrow COA_{n}^{*}$$
$$COA_{n}^{*} + COA_{n}^{*} \rightarrow Grafted\ Colocasia$$
$$A^{*} + A \rightarrow AA^{*}$$
$$A^{*}{}_{n-1} + A \rightarrow A^{*}{}_{n}$$
$$A^{*}{}_{n} + COH \rightarrow CO^{*} + A_{n}h\ (homopolymers)$$

Where COH stands for Colocasia gum, A stands for Acrylamide and MW stands for Microwave irradiation.

It is proposed that hydroxyl groups (being polar) of gum will absorb the microwave energy and will generate acrylamide radicals and Colocasia radicals. These free radicals will then further react with other molecules of gum to formulate the grafted gum till all the gum molecules get consumed. After that, acrylamide radicals react with each other to formulate the homopolymers in solution (Mishra *et al.*, 2011).

In this study, microwave-assisted grafting of Colocasia Esculenta was performed and explored by Box-Behnken Design Matrix, as shown in Table 2 and Table 3.

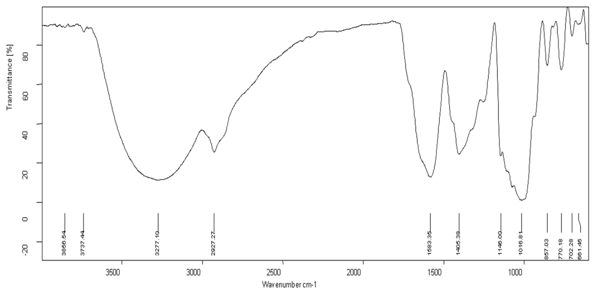

Figure 4: FTIR spectrum of Extracted Colocasia esculenta (Arbi)

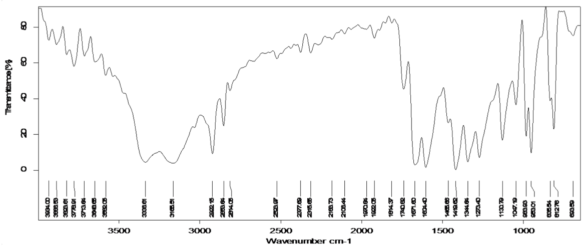

Figure 5: FTIR spectrum of acrylamide

In the Tables 2 and 3, X1, X2 and X3 were independent variables while Y1, Y2 and Y3 were dependent variables. This design provides the following non-linear quadratic equations.

$$\%Yield = 89.77460317 - 1.528826208.X_1 + 27.01927821.X_2 + 8.27795245.X_3 - 3.169763471.X_1.X_2 - 5.0505502105.X_1.X_3 - 13.47420635.X_2.X_3 - 10.09757453X_1^2 - 29.69895503.X_2^2 + 4.877923287.X_3^2$$

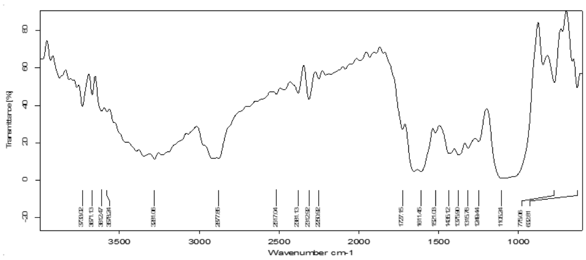

Figure 6: FTIR Spectrum of Grafted Colocasia esculenta (Arbi)

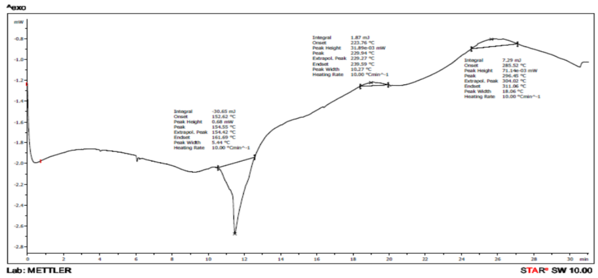

Figure 7: DSC of Extracted Colocasia esculenta

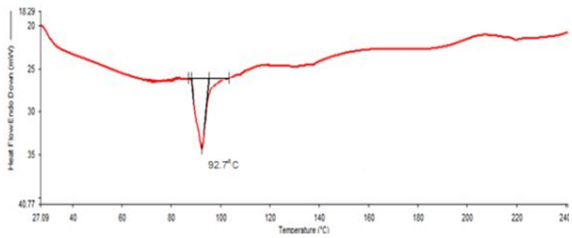

Figure 8: DSC of Acrylamide

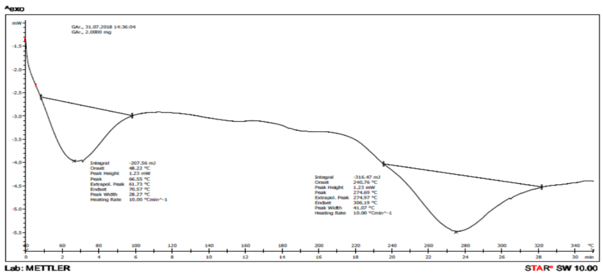

Figure 9: DSC of Grafted Colocasia esculenta (Arbi)

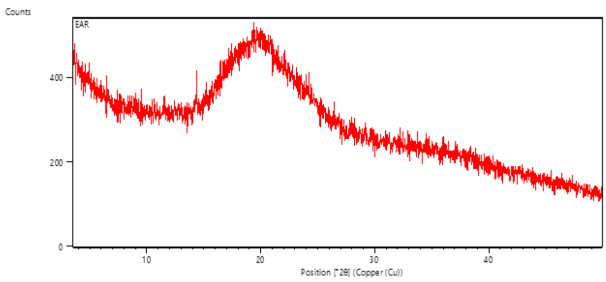

Figure 10: XRD analysis of acrylamide

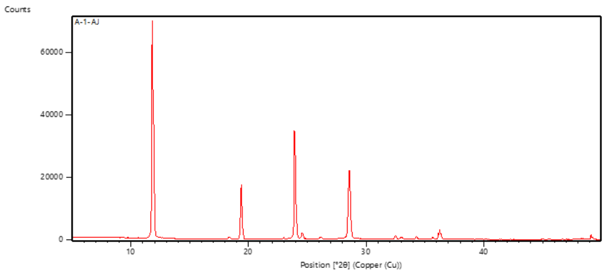

Figure 11: XRD spectra of extracted Colocasia esculenta

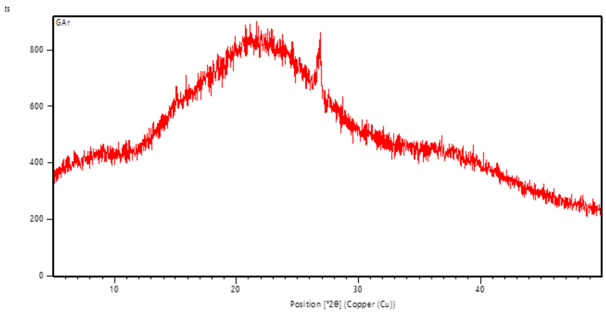

Figure 12: XRD spectra of grafted Colocasia esculenta

Figure 13: SEM Image of Colocasia Esculanta

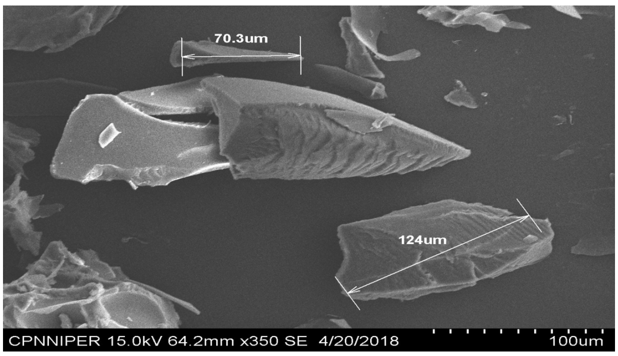

Figure 14: Scanning electron microscopy of Grafted Colocasia esculenta

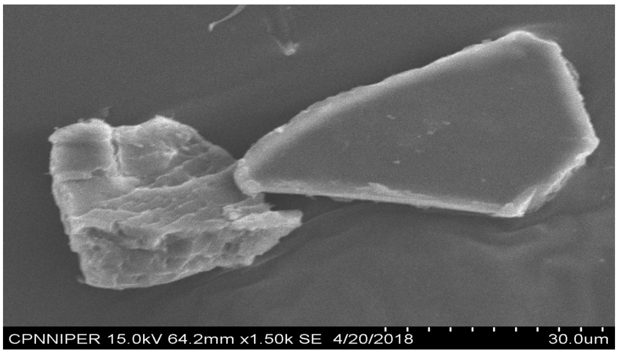

Figure 15: Scanning electron microscopy of Grafted Colocasia esculenta

$$\%Grafting = 37.3167 - 116.045X_1 + 151.7927X_2 + 48.87161.X_3 - 62.8188.X_1.X_2 - 37.5297.X_1.X_3 - 70.7396.X_2.X_3 - 14.8404.X_1^2 - 164.814.X_2^2 + 34.50339.X_3^2$$

$$\%Efficiency = 71.86774194 - 6.848537095.X_1 + 27.45767014.X_2 + 8.414123015.X_3 - 3.250274295X_1.X_2 - 5.13781348.X_1.X_3 - 13.69153226.X_2.X_3 - 9.917231478.X_1^2 - 30.17894567.X_2^2 + 4.957574704.X_3^2$$

Where X_1 is Concentration of gum, X_2 is Power, and X_3 is Irradiation time.

The model F-value of 91.507, 42.109 and 94.134 indicate about the significance of the model. "Prob>F" values are less than 0.05 indicates the significance of the model. The ratio of Pred R-squared to Adeq R-squared measures the noise ratio.

Response surface plots have explained the effects of different independent variables on dependent variables.

Figure 1a shows the effect of power, time of irradiation on % yield. It was observed that as with an increase in power, there would be a significant increase in % yield; however, with an increase in irradiation time, there was no significant effect on % yield. Figure 1b shows the effect of gum concentration and power on % yield. It was observed that power has a significant effect, and however, with an increase in concentration, % yield was increased initially after that. It became almost constant. Figure 1c shows the effect of gum concentration and irradiation time on % yield. It was observed that as the concentration was increased, the % yield was increased significantly up to a limit after that it became almost constant. However, with an increase in irradiation time, the % yield was increased gradually.

Similarly, Figure 2a, Figure 2b and Figure 2c show the effect of concentration, power and irradiation time on % grafting. It was observed that with an increase in power, there would be a maximum increase in % grafting. Even with the increase in irradiation time, the % grafting will also be increased significantly. In the case of concentration, the % yield slightly increases with increase in concentration up to a limit after that it becomes almost constant.

Figure 3a, b, c show the effect of concentration, power and irradiation time on % grafting efficiency. The results are almost the same as above. The maximum effect is of power on % Grafting efficiency while the minimum effect is of concentration.

Characterization of Colocasia-g-poly (acrylamide)

By using Design Expert, the optimized batch of grafted gum was selected. The formulation F_8 with % yield of 99.57, % grafting of 634.33 and % grafting efficiency of 87.49 was subjected to Fourier transform infrared spectroscopy, Differential scanning calorimetry, X-ray diffractometry and scanning electron microscopic studies.

FTIR Spectroscopy

Figure 4 shows the FTIR spectra of Colocasia esculanta with O-H stretching at 3277.10. The FTIR spectra of acrylamide (Figure 5) showed the stretching due to the presence of symmetric and asymmetric NH group. The FTIR spectra of grafted gum (Figure 6) showed a broad spectrum band at 3281.06 due to overlap of a hydroxyl group of colocasia and N-H band of monomer.

Differential scanning calorimetry

Figure 7 shows the DSC curve of Colocasia esculanta, which showed a broad spectrum sharp exothermic peak at 154°C. In contrast, broad endothermic peaks with low intensity were observed at 229°C and 296°C. Figure 8 shows the DSC curve of acrylamide. DSC curve of grafted Colocasia esculanta (Figure 9) showed a change in glass transition temperature. This can be seen with exothermic peaks at 66.5°C and 274°C.

X-ray diffraction

The XRD spectra of Colocasia esculanta (Figure 10) showed the amorphous nature because no characteristic was observed; however, XRD spectra of acrylamide (Figure 11) showed the characteristic peaks due to its crystalline nature. The XRD spectra of grafted gum (Figure 12) showed the less intense peaks as compared to acrylamide which confirms the grafting of acrylamide onto the gum.

Morphology

The morphology of the surface of Colocasia esculenta and grafted Colocasia esculenta was revealed by Scanning electron microscopic studies (Figures 13, 14 and 15). The roughness and unevenness on grafted Colocasia esculenta were due to grafting of polymer on the surface of gum during copolymerization with acrylamide.

CONCLUSION

Microwave-assisted grafting method has been used to synthesize Colocasia-g-polyacrylamide. Optimization was done by using Box Behnkan Design. The results revealed that microwave power, irradiation time and concentration of gum had a particular effect on % yield, % grafting and % Grafting efficiency. The Fourier transform infrared spectroscopy, Differential scanning calorimetry, X-ray diffractometry and scanning electron microscopic studies revealed the formation of a graft copolymer of Colocasia esculenta and acrylamide. So it may be concluded that microwave-assisted grafting has been used to modify the natural polymers and will improve their performance in different types of formulations.

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Declaration of Interest

The authors report no conflict of interest. The authors alone are responsible for the content and writing of this article.

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