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Research Article

Keywords: Orange Peel Powder (OPP), Antibacterial property, Silver nanoparticles, Filler material, Thermal property

Posted Date: June 16th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-239984/v1>

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Synthesis of Silver Nanoparticles through Orange Peel Powder for Antibacterial Composite Filler Applications

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Abstract

Environmental concerns and the positive aspects of biowaste materials gained the attention of researchers to use them as filler materials in fabricating of green composites along with polymer matrices, but most of them are not suitable for extensive applications in high thermal applications. In most of the natural particulate materials are not having the ability to fight against pathogens. To overcome such barriers, a modification of biowaste - Orange Peel Powder (OPP) by the generation of silver nanoparticles (AgNPs) is prepared with the one-step hydrothermal process. The modified Orange Peel Powder (MOPP), is then characterized by FESEM, EDX, FT-IR, XRD, and Thermal analyses. The presence of AgNPs in the MOPP is confirmed through FESEM & EDX analysis. FT-IR spectral analysis pronounced the non mutate functional groups in MOPP as compared with OPP. The generation of AgNPs in MOPP is confirmed through the XRD peaks of reflection planes at (1,1,1), (2,0,0), (2,2,0) & (3,1,1). Thermal Analysis results of TGA and DSC show the MOPP has increased thermal stability up to 363°C. Antibacterial test against Gram-negative and Gram-positive bacteria for OPP & MOPP shows the inclusion of Ag strongly objects the pathogens. Eventually, the MOPP can be utilized as filler material along with the polymer matrix in high thermal as well as antibacterial composite filler applications.

Graphical Abstract

Keywords

Orange Peel Powder (OPP), Antibacterial property, Silver nanoparticles, Filler material, Thermal property

Introduction

Majority of the agricultural wastes as well as municipal solid waste left unused and create problems to the environment and municipal solid waste management in countries like India and European countries[1]. Studies revealed that agricultural wastes of 200 million tons were generated in India alone and 998 million tons globally[2]. In that organic fruit waste of Cítricos del Andévalo Orange Juice processing company located in Spain contributes 400 tons every day even though they can be reused[3]. Organic fruits like Orange possess 50-60% of their total weight as waste in forms of peels, seeds and membrane residue. Orange peels contain 17.5% of cellulose, 8.5% of hemicellulose and Pectin[4]. The cognate chemical composition materials were reported by the researchers for various applications like *Ocimum sanctum* leaves with silver nanoparticles to form films for packaging application[5], *Chitosan* in plated with silver nanoparticles for the application of the natural rubber latex[6], *Acacia leucophloea* fibers for the design of lightweight materials[7], *Tamarind leaf* with silver nanoparticles used for the antibacterial textile materials[8], and *Pennisetum purpureum* grass formulated with copper nanoparticles for the application of dressing materials in the medical field[9]. With the above incentive, Orange Peels in the Powder form can be utilized for packaging applications in addition to the polymers matrices as a filler. To improve its utilization in large scope it can be modified by adding silver nanoparticles to involve the same in high thermal applications.. Silver nanoparticles (AgNPs) were generated from the aqueous silver nitrate solution (AgNO_3) and they possess good chemical as well as thermal properties[10],[29]. From the literatures, the lack of compatibility analysis of the biowaste materials are found, to utilize as a filler material especially along with silver nano particles. The antibacterial activity of the natural waste materials can be improved with the addition of AgNPs in order to improve its utilization as a filler material along with polymer matrix for the application of packaging films. By this inclusion of AgNPs the thermal properties of this biowaste materials can also be improved and also the utilization in the high thermal applications like packing foods to improve their shelf life.

In this investigation, OPP has been modified with silver nanoparticles by the hydrothermal process and the modified OPP (MOPP) is characterized and suggested that the MOPP can be used as a filler material for the high thermal green composite applications.

Materials And Methods

Materials

Orange Peel Powder (OPP) was procured from MG Naturals, Chennai, Tamil Nadu with the size of less than 50 μm . The ultrapure grade of silver nitrate (AgNO_3) was purchased from Modern Scientific company, Madurai, Tamil Nadu and used as procured.

Preparation of Modified Orange Peel Powder (MOPP)

The preparation of MOPP was done by the procedure described elsewhere[11] [30]. Briefly, The 3grams of OPP was added to the 50ml of 5mM aqueous solution of AgNO_3 and stirred with a magnetic stirrer for a period of 24hours at the temperature of 80°C. The modification of OPP can be observed by coloration change from pale yellow to dark brown. Then the MOPP separated and dried in the oven for 3hrs at the temperature of 100°C.

Characterization of Nano composite Bio film

Microscopic Analysis (FESEM)

The morphological study of AgNPs in MOPP had been evaluated by the images of FESEM and EDX spectra through Carl Zeiss- Sigma with Gemini column at a magnification of 1 μm and operated at 20kV. The experiment is to analysis the distribution of silver nanoparticles in the MOPP

FTIR Analysis

The functional groups in the MOPP & OPP are determined through the FT-IR spectrum recorded by Perkin-Elmer 783. The spectrophotometer in the range of 4000 cm^{-1} to 500 cm^{-1} with 4 cm^{-1} resolution and 45 scans for both the case using KBr pellets.

X-ray Diffraction Analysis (XRD)

To record the x-ray diffractogram of MOPP and OPP, to analyse the materials present as well as plane of reflection in both OPP and MOPP the EXPERT-PRO diffractometer system was used with the generator setting of 30MA, 40KV. The anode material was Cu and the position in the range of $2\theta = 10^\circ$ to 80° . The reflection planes of AgNPs presented in the MOPP had been calculated by,

Bragg's law

$$d = \frac{\lambda}{2\sin\theta}$$

and

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (1)$$

Thermogravimetric Analysis (TGA)

The thermogravimetric analysis for MOPP & OPP was carried out on NETZSCH STA 2500 Regulus instrument with the temperature range of 30°C to 550°C at 10 °C/ min heating rate at an nitrogen atmosphere with a flow rate of 20ml/min. From the TGA, thermal stability of OPP and MOPP were obtained. To obtain the derivative form of thermo gram the differentials of primary thermogram was calculated by central finite difference method [12] i.e.,

$$DTG = (W_{t+\Delta t} - W_{t-\Delta t})/2\Delta t \quad (2)$$

where,

$W_{t+\Delta t}$ & $W_{t-\Delta t}$ are residual weight samples at $t+\Delta t$ and $t-\Delta t$ time,

and Δt is time for reading sample residual weight

Kinetic activation Energy

The Broido's kinetics equation was used to determine the Kinetic activation energy through [13] [31],

$$\ln \left[\ln \left(\frac{1}{y} \right) \right] = - \left(\frac{E_a}{R} \right) \left[\left(\frac{1}{T} \right) + k \right] \quad (3)$$

Where,

R- Universal gas constant (8.314 J/mol.K); T-Temperature in K; E_a -Kinetic activation energy

K-reaction rate constant

$y = \frac{W_t}{W_o}$ Where, W_t - Weight at Time 'T'; W_o - Weight at Initial

The Broido's Plot between $\ln \left[\ln \left(\frac{1}{y} \right) \right]$ & $(1/T)$ used to determine the kinetic activation energy.

Differential Scanning Calorimetry (DSC)

DSC was performed to find glass transition tempertaure of both OPP & MOPP, on NETZSCH STA 2500 Regulus instrument at a heating rate of 10 K/ min under Nitrogen atmosphere by following ASTM E-967 ASTM 2008a and ASTM E-968 ASTM2008b standards [10],[32].

Result and Discussion

Microscopic Analysis (SEM) & EDX Spectra

Figure 1(a) shows the Scanning Electron Microscopic image of MOPP. Figure 1(b) represents the EDX spectra recorded from the SEM image.

Fig. 1 (a) SEM Image of MOPP (b) EDX Spectra of MOPP

In Figure 1(a), the spherical shape particles indicates the in-situ generates AgNPs which are marked in arrow heads. From Figure 1(b) the EDX spectra peak corresponding to 2.98 KeV~3 KeV value in the X axis confirms the presence of Ag in the MOPP along with C and O. The presence of C and O is confirmed through the peaks at 0.2 and 0.3 KeV respectively[19],[33].

FTIR Analysis

The FTIR spectra ranges from 4000 cm^{-1} to 500 cm^{-1} for MOPP and OPP are shown in Figure 2 to observe the chemical groups present in them. In this observation, the spectra of MOPP and OPP showed a broad band between 3500 cm^{-1} to 3100 cm^{-1} assigned to O-H stretching (hydroxyl groups). The peak at 2992 cm^{-1} wave number recognized to -C-H- stretching vibration of alkenes[14]. The absorption bands at 1741 cm^{-1} and 1622 cm^{-1} represented C=O stretching present in hemicelluloses [7] and -C=C- stretching respectively. The 1521 cm^{-1} arise due to the C=C ring stretching (Aromatic group). 1438 cm^{-1} peak observed due to carbonyl stretching raise in lignin[15]. The bands at finger print region, 1016 cm^{-1} clarified the C-O-C vibrational stretching of polysaccharides[11] and 838 cm^{-1} confirmed the presence of glucosidic (β) linkages between hemicelluloses and cellulose sugar units[7]. The C-OH bending in cellulose observed through peak at 598 cm^{-1} [16],[34]. From the Figure 2 it is conspicuous that there is slight shift in the peaks of MOPP as compared to the OPP such as 2924 cm^{-1} to 2992 cm^{-1} , 1743 cm^{-1} to 1741 cm^{-1} , 1612 cm^{-1} to 1622 cm^{-1} and 1016 cm^{-1} to 1018 cm^{-1} likewise the intensity of those peaks lowered in the MOPP due to reduction of silver ions to AgNPs (Ag^+ to Ag) but it clearly evident that the minor shift in peaks

does not affected the functional groups present in the OPP during synthesis of AgNPs. The shift in the peaks as well as reduction in the intensity of the peaks are due to the involvement of functional groups in the synthesis of AgNPs. The results of FTIR spectral also revealed that no chemical interaction between AgNPs and OPP during preparation of MOPP[17].

Fig. 2 FTIR spectra of OPP & MOPP

X-ray Diffraction Analysis (XRD)

X-ray diffractogram of MOPP and OPP are presented in Figure 3. It is evident that the presence of two common peaks at $2\theta = 14.1^\circ$ and 21.5° , which are due to the reflection planes (1 0 0) of cellulose-I present in the OPP & MOPP[5]. These peaks were most likely to be exhibited in natural materials. In MOPP X-ray diffractogram in addition to above two peaks, peaks at $2\theta = 37.9^\circ$, 44.4° , 64.3° & 77.2° were observed. With the help of Bragg's law represented as equation (1), reflection planes of those peaks were found to be (1,1,1), (2,0,0), (2,2,0) & (3,1,1) of

AgNPs respectively[15]. These peaks and planes of reflections are well-matched with the ICDD (International Centre for Diffraction Data) PDF (Powder Diffraction File) 04-0783 for Ag[20].. Thus the MOPP has the silver nano particles in it (AgNPs).

Fig. 3 X-ray Diffractogram of OPP & MOPP

Thermogravimetric Analysis (TGA)

TGA analysis is for analyzing the thermal stability based on the weight loss of the material with the increase of temperature. DTG curves are derived using equation (2). Figure 4(a) and (b) showed the TGA and DTG thermograms of MOPP and OPP. Three stages of thermal degradations observed in both the powders, clearly through DTG curves. The initial degradation found to be identical for both MOPP & OPP at 100°C with weight loss of 4.27% for

MOPP and 6.22% for OPP with the effect of moisture evaporation. The intermediate degradation observed at 232°C for OPP & 246°C for MOPP with the higher weight loss by MOPP with 7.96% where as OPP exhibited 5.87% due to the degradation of pectin, hemi cellulose and links of cellulose [18]. The final degradation between 250°C to 400°C, the higher mass reduction of the MOPP & OPP observed because of complete degradation of cellulose. The mass loss observed at 400°C for MOPP is 48.7% and for OPP is 54.1%. There is a change in the point of inflection observed in MOPP as compared to OPP due to the inclusion of thermally stable AgNPs. The MOPP thermally stable up to 363°C where as thermal stability of OPP is 357°C. The residual mass of MOPP observed as 35% but OPP exhibited 24% of residual mass at 548°C. The higher residual masses of MOPP is due to the inclusion of high thermal withstanding capacity AgNPs.

Fig. 4 (a)TG - Curves of OPP & MOPP (b) DTG thermo grams of MOPP & OPP

Kinetic Activation Energy

It is the minimum energy required to start the degradation of the samples and are calculated from the equation (3), the activation energy for the thermal degradation of the MOPP & OPP in the temperature region of 200°C to 375°C was evaluated[21]. Figure 5 (a) and (b) shows the plot between $\ln \left[\ln \left(\frac{1}{y} \right) \right]$ and $(1/T)$ for the OPP& MOPP. The slope value of the generated straight line related to the activation energy in order to understand the thermal degradation of both the materials[22],[23]. The activation energy (E_a) of OPP is 71.50 KJ/mol which is increased to

91.10 KJ/mol in the case of MOPP. The aforementioned increase in activation energy is due to the effect of AgNPs present in the MOPP.

Fig. 5 Broido's Plot of (a) OPP & (b) MOPP

Differential Scanning Calorimetry (DSC)

DSC curves of the OPP & MOPP are presented in the Figure 6. DSC curve of OPP has a broad endothermic curve initially up to 100°C due to the decomposition of water present in them. OPP exhibits endothermic curves shows a two melting point peaks (T_{m1} & T_{m2}). T_{m1} corresponds to the degradation of hemicelluloses at around 230°C and the T_{m2} showed the degradation of cellulose at 347°C[24]. Glass transition temperature (T_g) of the OPP is around 80°C. Moreover exothermic cures of MOPP showed the enhanced melting points T_{m1} & T_{m2} in correspondence to the degradation of hemicelluloses and cellulose[25],[26]. The T_{m1} of MOPP observed at 250°C and T_{m2} at 362°C. Likewise the glass transition temperature of MOPP is improved to 102°C. The results ascribed the generated AgNPs improves the thermal behavior of the MOPP.

Fig. 6 DSC thermo grams of OPP & MOPP

Antibacterial Test

Both OPP and MOPP were tested against *P. aeruginosa*, *E. Coli* (Gram-negative) and *S. aureu*, *S. oralis* (Gram-positive) bacteria. The antibacterial activities of the OPP and MOPP are assessed based on the zone of inhibition in the agar plate showed in Figure 7. The large zone of inhibition relates to the strong antibacterial activity of the samples[27],[28]. The inhibition zones of OPP and MOPP against pathogens are listed in Table 1. The OPP powder posses a partial inhibition zone in the range of 13.5 mm to 17.4mm whereas the MOPP showed the strong inhibition zones from 37.4mm to 39.0mm of diameter because of the silver nanoparticles present in them. This implied that the MOPP has the ability against pathogens due to the antibacterial activity of AgNPs nature.

Fig. 7 Zone of inhibition formed by OPP(A1) and MOPP(A2) against (a) *E. coli*, (b) *P. aeruginosa*, (c) *S. aureus* and (d) *S. oralis*

Sample (Code)	Diameter of inhibition zone (mm)			
	Gram-negative		Gram-positive	
	<i>E. Coli</i>	<i>P. aeruginosa</i>	<i>S. aureus</i>	<i>S. oralis</i>
OPP (A1)	15.5 ± 0.5	17.4 ± 0.4	13.5 ± 0.5	15.6 ± 0.7
MOPP (A2)	38 ± 0	37.4 ± 0.8	38.5 ± 0.3	39.0 ± 0.1

Table 1 Antibacterial activity of OPP and MOPP

Conclusions

Owing to stretch the applications of biowaste filler materials, the modification of the OPP was done with the hydrothermal process for the in-situ generation of silver nanoparticles(AgNPs). The MOPP was characterized using SEM, EDX, FT-IR, XRD and Thermal Analysis. The presence of silver nanoparticles in MOPP was identified through SEM and EDX. Further, no change in the functional groups of MOPP was observed during the generation

of AgNPs by FT-IR analysis. The XRD result confirmed the presence Ag by the peaks mentioned by the ICDD. The generated AgNPs improved the thermal behavior of the MOPP by increased thermal stability up to 363°C and Kinetic activation energy of 91.10 KJ/mol. Likewise, the glass transition temperature is also improved to 102°C. The zone of clearance produced against gram- negative and gram-positive bacteria by MOPP represents the strong antibacterial activity as compare to OPP. With the above results the MOPP can be act as a filler material along with the polymer matrices for the fabrications of green composites in high thermal as well as antibacterial applications.

Acknowledgements

Authors are thankful to managements of both Kamaraj College of Engineering & Technology, Virudhunagar 626 001, Tamil Nadu, India, and Nehru Institute of Engineering & Technology, Coimbatore-641 105, Tamil Nadu, India for their support and encouragement.

Conflict of Interest

There is no conflict of interest among the authors.

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