International Journal of Current Advanced Research
ISSN: O: 2319-6475, ISSN: P: 2319-6505, Impact Factor: 6.614
Available Online at www.journalijcar.org
Volume 7; Issue 9(C); September 2018; Page No. 15416-15419
DOI: http://dx.doi.org/10.24327/ijcar.2018. 15419.2813

Research Article

SYNTHESIS OF RESORCINOL-FORMALDEHYDE POLYMER MICROSPHERES BY SPRAY DRYING TECHNIQUE

Sameer Wagh*., Pawan Gawali., Ashish Mohare and Dhananjay Balbudhe

Department of Plastics and Polymer Technology, Laxminarayan Institute of Technology, Nagpur-440033, Maharashtra, India

A R T I C L E I N F O

Article History:

Received 15th June, 2018
Received in revised form 7th July, 2018
Accepted 13th August, 2018
Published online 28th September, 2018

Key words:

Spray dryer, hollow polymer microsphere, Resorcinol-formaldehyde resin.

A B S T R A C T

Spray drying is a widely used industrial process involving formation of solid particles from liquid feed, which has many applications in areas including food, pharmaceutical, ceramic, polymer, and chemical industries. In this present work, Resorcinol-Formaldehyde hollow polymer microspheres were synthesized using spray drying technique and particle size of hollow polymer microspheres was in the range of 2-10µm. To obtain desired properties of hollow polymer microspheres various operating parameters like flow rate and temperature, were optimized. This polymer microspheres have many practical applications in the drug delivery system, synthetic foams, catalysis, fillers etc.

INTRODUCTION

In recent years, hollow microspheres are found to be one of the most attractive functional carbon or polymer microspheres because of their unique properties. One of the interesting and potential applications of such microspheres is in controlled drug delivery system in the pharmaceutical field and biomedical applications, artificial cells, forming of light weight syntactic foams, fillers, thermal insulators etc. Over the past decade, extensive research has been carried out in the preparation of hollow microspheres, because their special characteristics such as the interior void space, low density and good flow properties.[1] These materials have been successfully used as fillers for low-weight, mechanically and thermally stable engineering materials, such as metal, thermal insulators and structural foams in the aerospace thermal protection system. Due to their light weight they are also used in aerospace industry for weight sensitive materials [1].

Spray drying technique is a fast continuous unit-operation having great importance in chemical engineering and technology. Spray drying process is widely used in the food industry. But over past decade it is used in many chemical industries. Examples of spray-dried products from this industry are biomedical and pharmaceutical drugs, washing powders, detergents, catalysts, polymers, colour pigments and variety of dried salts. A reason for the application of spray-drying is that it is one of the most efficient methods, by which a liquid solution can be converted to a solid particles of micro or nano scale. There are different methods for removal of water from such solutions such as freeze drying or liquid-liquid extraction which uses solvents for extraction but it is quite uneconomical and undesirable processes. By spray-drying, powders of desired functional properties can be obtained.

RF reactions gives either novlac or resol depending upon the formaldehyde to resorcinol ratio. RF resins finds its applications in wood adhesives but is not widely used because of its instability and high cost [6].

In this work, Resorcinol-formaldehyde (RF) hollow polymer microspheres (HPMs) was synthesized using spray drying technology. Resorcinol-formaldehyde precursor solution was spray dried and the solvent (water) was removed rapidly in spray dryer and RF resin solid powder was collected at the end. For better efficiency, various process parameters like feed flow rate, inlet and outlet temperature were optimized. The Characterization was carried out of RF microspheres to study the morphology of the product along with various tests are performed to study its chemical and physical properties. This given method for production of RF hollow polymer microspheres is rapid, efficient and low cost and have many practical applications in drug delivery, catalysis, pollution control, aerospace, fillers etc.

Experimental Section

Materials

Resorcinol(R), Formaldehyde solution (37%) (F), Sodium bicarbonate ($NaHCO_3$), polyvinyl alcohol (PVA).

Corresponding author:* **Sameer Wagh
Department of Plastics and Polymer Technology, Laxminarayan Institute of Technology, Nagpur-440033, Maharashtra, India

Synthesis of RF hollow polymer microspheres

For preparation of RF resin microsphere, solution of resorcinol and formaldehyde (1:3 mole ratio) in presence of NaHCO3 was prepared. The solution was diluted using distilled water up to the required extent. Then it was sprayed through spray dryer at inlet temperature of 200°C and flow rate 540 mL/h. The solvent (water) was removed rapidly in spray dryer and RF resin solid powder was collected at the end. Now for the preparation of hollow microspheres, aqueous solutions of the precursor were prepared by mixing resorcinol (R), formaldehyde (F) and a small amount of Polyvinyl Alcohol (dissolved PVA) in the presence of $NaHCO_3$ with continuous magnetic stirring after which the solution was further diluted with distilled water to the desired concentration. The mixed solution was stirred for 1.5 h at 50 °C. Then prepared precursor solution was spray dried using a spray dryer. The solution was pumped into atomizer at the rate of 540 mL/h, together with a constant spray air flow. The inlet temperature was set to 200 ^{0}C generally. HPMs were discharged continuously from the drying chamber and then collected using a cyclone separator.

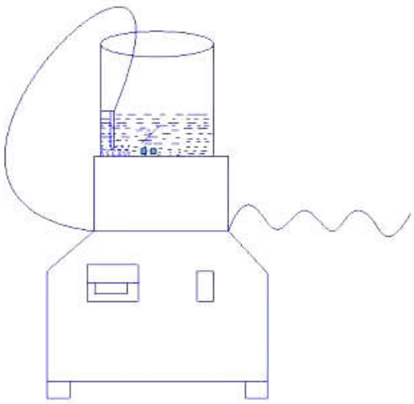


Fig 1 Experimental setup of precursor solution

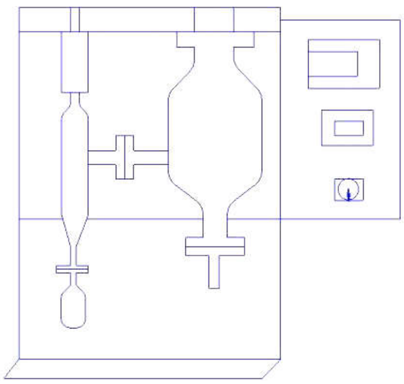


Fig 2 Schematic representation of spray dryer

Testing and Characterization

Viscosity of RF precursor solution

The viscosity RF precursor solution was determined at different time while heating at constant temperature using Ford cup viscometer. The viscosity was reported in seconds. It is important when using a Ford Cup and when retesting liquids, that the temperature of the cup and the liquid is maintained, as ambient temperature makes a significant difference to viscosity and thus flow rate.

Adsorption test

To test the adsorption ability of the porous RF microspheres, the methylene blue (MB) alcohol solution was taken as the adsorption model.

Characterization

The morphology of RF microspheres was studied by scanning electron microscope (SEM). The electron beam is scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometre (nm).

Functional group present in final polymer product was determined using Fourier transformation infrared spectroscopy (FTIR). The absorbance or transmittance intensity was recorded in percentage as a function of wave number (cm-1). Phase transitions and thermal stability of RF polymer microspheres was examined using thermogravimetric analysis (TGA). The amount of weight change of a material was reported either as a function of increasing temperature or time.

Ultraviolet–visible spectroscopy or ultraviolet-visible spectrophotometry (UV) was performed on RF HPMs which refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region.

RESULTS AND DISCUSSION

Effect of time and temperature on viscosity

The precursor solution was prepared and its viscosity was determined using ford cup. After 1 hour with continuous heating, its viscosity was reduced to certain level as viscosity is inversely proportional with temperature. But after 1 hour reaction was started, so there was rise in viscosity of solution as jelly formation starts with reaction. Colour of the solution changed from yellow to reddish brown. If the precursor solution is kept for 24 hour at room temperature, there is still rise in viscosity because reaction is started at room temperature.

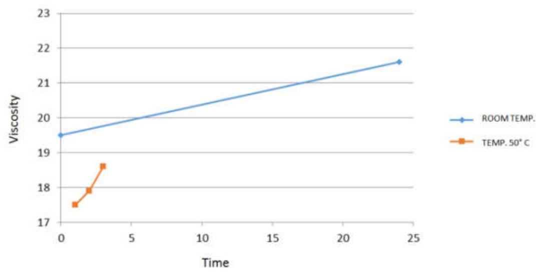


Fig 3 Effect of time on Viscosity

Adsorption test

As shown in Fig. 4, the Hollow polymer Microsphere showed a good adsorption ability, which may be useful as absorbents for adsorbing large poisonous molecules, drug delivery, and pollution removal.

t=0 t=2 hour

(a) (b)

Fig 4 Adsorption test of the porous RF microspheres; (a) before adsorption (b) after adsorption

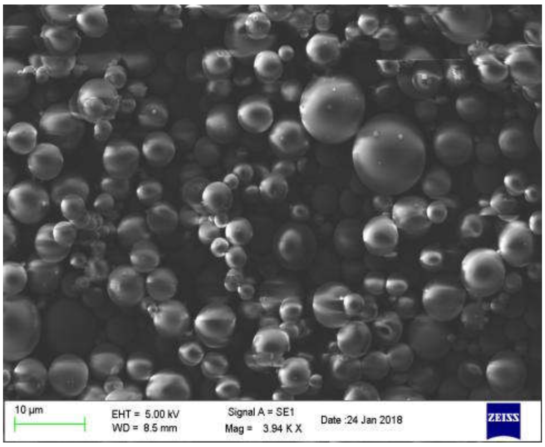
Characterization

Scanning electron microscopy (SEM)

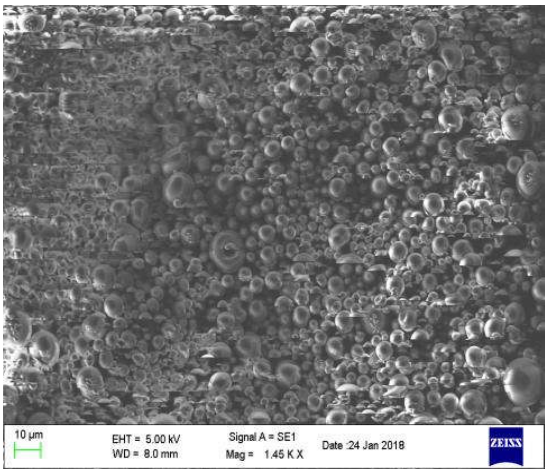
Table 1 Comparison of SEM images of RF resin at different flow rates

Sample	Flow Rate	Temperature (°C)	Diameter (µ)
RF Resin	40%	200	2-10
RF Resin	40%	200	2-10
HPMs	50%	200	2-10

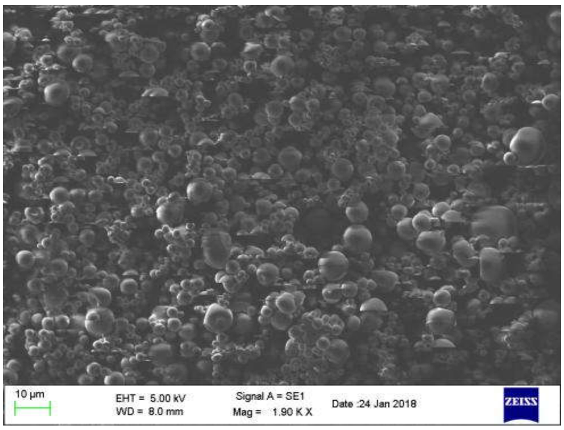
The morphology of the RF microspheres was examined by scanning electron microscope (SEM). The sphericity of microspheres was good.



a)



b)



c)

Fig 5 SEM images a) RF resin at 40 % flow rate b) RF resin at 50% flow rate c) HPMs

The product morphology is also strikingly depended on process conditions such as inlet temperature and feed speed. The morphology of particle was "spherical" in nature and its particle size was in the range of 2-10 µm. There was no such notable change in morphology of particle in fig. 5a, fig.5b and fig. 5c.

Fourier transformation infrared spectroscopy (FTIR)

Below graph (fig.6) shows the FTIR spectrum of RF microsphere polymer.

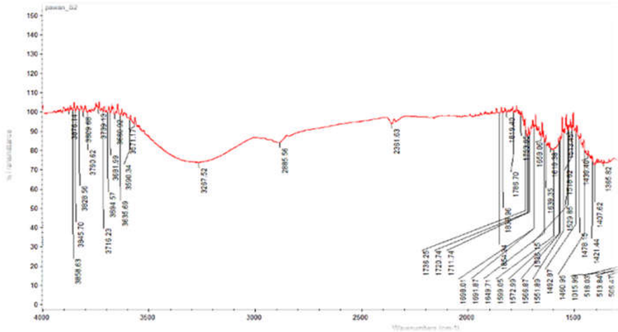


Fig 6 FTIR spectra of RF resin microsphere

The spectrum was characterized by a broad band of OH stretching at 3300-3600 cm^{-1} and bands at 2800 cm^{-1} and 3000 cm^{-1} due to in-plane and out-of-plane aliphatic stretching, respectively. The absorption bands at 2100 cm^{-1} and 2200 cm^{-1} was assigned to aromatic ring i.e. benzene ring. The band at 1200-1300 cm^{-1} was assigned to C-O of phenolic structure. Saturated CH_2 linkages was observed commonly in the region of 2351 cm^{-1}.

UV Spectroscopy

Fig. 7 shows UV spectra of water dispersed solution of RF microspheres was prepared before one week & fig. 8 shows UV spectra of resorcinol formaldehyde resin with concentration 1gm/100 ml of water (freshly prepared).

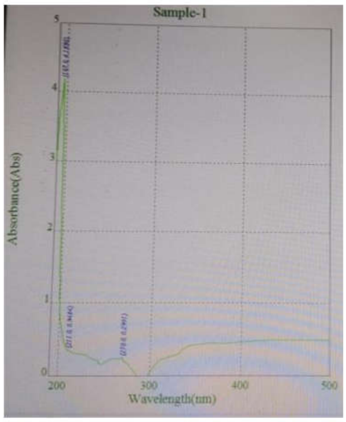


Fig.7 UV spectrum of water dispersed solution of RF resin microspheres

It is shown that maximum absorption peak occurs at 271 nm in fig. 8 representing an aromatic ring which is in good agreement with literature [5] where maximum absorption for resorcinol occurs within wavelength range 270-294 nm. In fig. 7 maximum absorption peak occurs at 197 nm, this may be due to degradation of product.

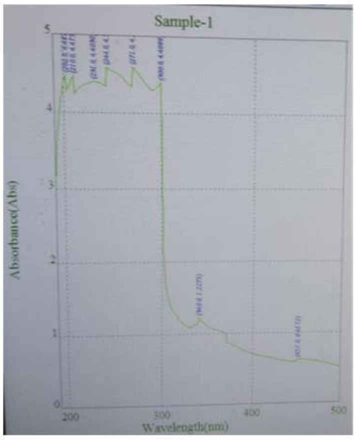


Fig 8 UV spectrum of RF resin microspheres

Thermogravimetric analysis

The thermal stability of RF resin was evaluated using TGA. The sample does not lose its weight until it reaches the temperature of 250°C at constant heating. It means that the product can be used up to 200°C. This process consist of different stages like heating, removal of small terminal group from polymer structure, decomposition of methylene bridges and finally complete degradation. Product started decomposing above 250°C with continuous weight loss. Finally at 800°C, the product was completely burnt and vanished.

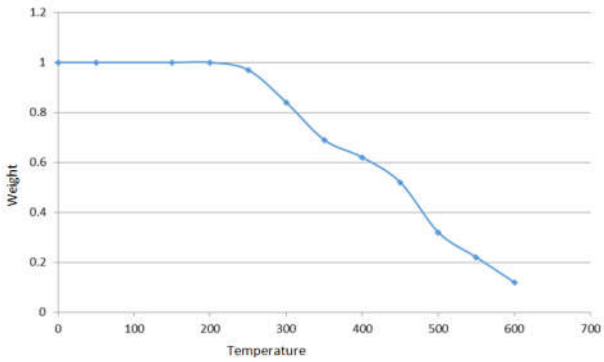


Fig 9 Thermogravimetric analysis of RF resin

CONCLUSION

Spray drying is a rapid and efficient technique for the synthesis of resorcinol-formaldehyde (RF) hollow polymer microspheres (HPMs). The particles size of HPMs in range of 2-10 µm can be produced by this method. Effects of precursor composition and operating conditions on morphology and purity of the RF microspheres was studied to determine best method for producing HPMs. The advantages for this spray drying technique for RF HPMs is, it's less time consuming and low cost and hence it is economically feasible for practical use. These Resorcinol-formaldehyde hollow polymer microspheres have great numerous potential applications in catalysis, synthetic foams, adsorption, drug delivery, electrode materials, fillers etc.

References

1. Jianguo Zhou, Hongyang Zhao, Jitong Wang a, Wenming Qiao, Donghui Long,Licheng Ling, Scalable preparation of hollow polymer and carbon microspheres by spray drying and their application in low-density syntactic foam, Materials Chemistry and Physics, 181 (2016) 150-158.
2. Jianmei Wang, Xiaowen Huang, Pei Zhao, Xueying Wang, Ye Tian, Chengmin Chen,Jianchun Wang , Yan Li, Wei Wan, Hanmei Tian, Min Xu, Chengyang Wang, Liqiu Wang, On-Chip Facile Preparation of Monodisperse Resorcinol Formaldehyde (RF) Resin Microspheres, *MDPI,(2018).*
3. Shaheen A.Al -Muhtaseb, James A. Ritter, Preparation and Properties of Resorcinol-Formaldehyde Organic and Carbon Gels, Adv. Material, 15 (2003) 101-114.
4. Shiv K. Sharma, Natural Fiber Reinforcement into Formaldehyde-Resorcinol Thermosetting Resin, researchgate (2013).
5. S M Attia, M S Abdelfatah,M M Mossad, Characterization of pure and composite resorcinol formaldehyde aerogels doped with silver, *Journal of Physics*, 869 (2017).
6. Tohong li, Ming Cao, Jinankun Liang, Xiaoguang Xie, Guanben Du, Mechanism of base-catalyzed Resorcinol-Formaldehyde and Phenol-Formaldehyde condensation reactions: A theoretical study, Polymers 2017, 9, 426.
7. Wei Bin, Wang Shujun, Song Hongguang, Liu Hongyan, Li Jie, Liu Ning, A review of recent progress in preparation of hollow polymer microspheres, Pet.Sci.6 (2009) 306-312.

How to cite this article:

Sameer Wagh *et al* (2018) 'Synthesis of Resorcinol-Formaldehyde Polymer Microspheres By Spray Drying Technique', *International Journal of Current Advanced Research,* 07(9), pp. 15240-15244. DOI: http://dx.doi.org/10.24327/ijcar.2018. 15419.2813

****