Journal of Physics and Chemistry of Solids 104 (2017) 169–174

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Synthesis and characterization of polypyrrole grafted chitin

A.T. Ramaprasad[a,*], D. Latha[b], Vijayalakshmi Rao[c,*]

[a] Department of Engineering Physics, Alva's Institute of Engineering and Technology (affiliated to Visvesvaraya Technological University, Belagavi), Moodbidri, 574225 Mangalore, Karnataka, India
[b] Department of Engineering Physics, Sree Devi Institute of Technology, Kenjar, 574142 Mangalore, Karnataka, India
[c] Department of Materials Science, Mangalore University, Mangalagangotri, 574199 Mangalore, Karnataka, India

ARTICLE INFO

Keywords:
Chitin
Polypyrrole
Grafting
Conducting polymer

ABSTRACT

Synthesis and characterization of chitin grafted with polypyrrole (PPy) is reported in this paper. Chitin is soaked in pyrrole solution of various concentrations for different time intervals and polymerized using ammonium peroxy disulphate (APS) as an initiator. Grafting percentage of polypyrrole onto chitin is calculated from weight of chitin before and after grafting. Grafting of polymer is further verified by dissolution studies. The grafted polymer samples are characterized by FTIR, UV–Vis absorption spectrum, XRD, DSC, TGA, AFM, SEM and conductivity studies.

1. Introduction

Five-member heterocyclic compounds such as, polypyrrole, polythiophene, etc. are very interesting due to their potential applications in the field of energy storage [1–3], sensors [4–6], electronic and optical devices [7] and so on. Among conducting polymers, polypyrrole has been one of the most studied polymers because of its physical and electrical properties that have led to several applications such as, solid state devices and electronics [8]. However, due to its poor mechanical properties, for example, brittleness and low level of processability constitute major obstacles to its extensive applications [9]. To improve the structural and physical properties, several blends or composite materials containing PPy were prepared [10–13]. Improvements are expected from composite materials in which the conducting polymer contributes to the required conducting behavior, while the other polymer enhances the mechanical properties. Thus, to create new polymeric materials with specific electrical properties, a combination of a conventional polymer with conductive polymer is made.

In this article an attempt has been made to graft polypyrrole onto chitin. Our desire to exploit the properties of chitin and polypyrrole has led us to study chitin-polypyrrole graft system. Chitin is a polysaccharide composed of β-(1, 4) linked 2-deoxy -2-acetamido-D-glucopyranose and partially of β-(1, 4) linked 2- deoxy-2-amino-D- glucopyranose [1,2,14–18]. The structure of chitin is as shown in Fig. 1. It is the most abundant natural polymer after cellulose, commonly found in exoskeleton or cuticles of many invertebrates and in the cells of most fungi and some algae. Because of important advantages such as biocompatibility, biodegradability, high mechanical strength, non toxicity etc chitin and its deacetylayted form chitosan have attracted attention of several researchers [1,2,14–18].

Polypyrrole is one of the important conducting polymers because of its good electrical conductivity, good environmental stability and relative ease of synthesis either by electrochemical polymerization [14,15] or by chemical oxidative polymerization [16]. Both the electrochemically prepared PPy films and the chemically prepared PPy powders are black in colour. PPy is stable and has good conductivity, but it is a hard and brittle material thus possess low processability [17]. Its mechanical properties can be enhanced by incorporating this conducting polymer with one or more conventional polymers either by blending or grafting and these studies were extensively reviewed by Mária Omastová and Matej Mičušík [18]. The structure of Polypyrrole is shown in Fig. 2.

2. Experimental section

2.1. Materials and chemicals

Chitin from HIMEDIA Mumbai with molecular weight 400,000 g/mol, Ammonium peroxy disulphate (APS), N, N Dimethyl acetamide (DMA), LiCl all GR grade from MERCK were used as received. Pyrrole AR grade from SRL was distilled under reduced pressure before use.

2.2. Sample preparation

2 g of chitin was soaked in pyrrole solution of various concentrations (0.1 M, 0.3 M & 0.5 M) in 0.1 M HCl for 24hrs. Above solution

* Corresponding authors.
E-mail addresses: ramaprasadat@rediffmail.com (A.T. Ramaprasad), vijrao@yahoo.com (V. Rao).

http://dx.doi.org/10.1016/j.jpcs.2017.01.017
Received 14 July 2016; Received in revised form 7 December 2016; Accepted 14 January 2017
Available online 17 January 2017
0022-3697/

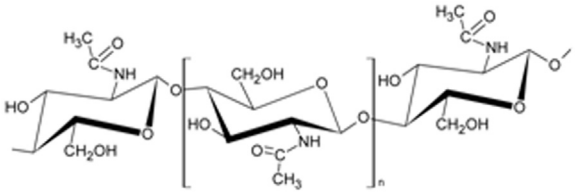

Fig. 1. Structure of Chitin.

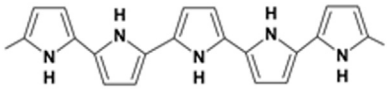

Fig. 2. Structure of polypyrrole.

was filtered and the soaked chitin was transferred to APS solution in equimolar amounts prepared in 1 M HCl. The reaction was carried out for 16 h. The resultant graft polymer was filtered and dried in hot air oven at 75 °C for 12 h. Sample was stored in vacuum desiccator and used for further characterization.

2.3. Measurements

0.5% of graft solutions were prepared using DMA/LiCl as solvent and UV–Vis absorption spectra were recorded between 300 and 800 nm using spectrophotometer (Shimadzu:model UV-3101 PC). XRD measurements were carried out using a X-ray diffractometer (Bruker D8 Advance). The angular range was from 7 to 40° (2θ), throughout the entire course of investigation. For electrical measurements, the grafted samples were dissolved in DMA/LiCl, and filtered. The free standing films were obtained by transferring the solution onto a glass plate and the solvent was dried. The films were mounted between two silver electrodes in a sample holder for conductivity measurements. For this purpose, current was measured by applying voltage across the films by using Keithley electrometer (model 6517A). The FT-IR spectroscopic analysis for the samples were done by Perkin Elmer FTIR spectrophotometer (model 1725X) using KBr disc. The scanning was ranged from 4000 cm^{-1} to 400 cm^{-1}. TGA and DSC analysis was carried out using Perkin Elmer, Diamond TG/DTA machine, in nitrogen atmosphere, from40°C to 630 °C at 10 °C/min. SEM and AFM photographs were taken using Scanning Electron Microscope (Model: JEOL JSM 5800CV) and AFM machine respectively.

3. Results and discussion

All samples prepared are black in colour, which is the preliminary confirmation for the formation of PPy on chitin matrix. Further grafting of PPy is confirmed by dissolution studies. Pure PPy is insoluble in DMA or DMA /LiCl solvent systems, but grafted polymer is soluble in DMA/LiCl solvent system in which chitin is soluble. The black colour of the solution further confirms the penetration of PPy on to chitin matrix. Also grafted samples take more time for gelation when compared to pure chitin. From the initial and final weights of polymer before and after grating, percentage of grafting was calculated. Percentage of grafting is given by the expression.

$$PG = \frac{W_i - W_f}{W_i} \quad (1)$$

where W_i is the initial weight before grafting and W_f is the final weight after grafting. Table 1 presents percentage of grafting with pyrrole concentration. From the Table 1 it is seen that percentage of grafting increases as the pyrrole concentration increases.

On the basis of preliminary electrical studies, the conductivity of CP3 chitin-PPy graft is found to be more than CP1 chitin-PPy graft and CP5 chitin-PPy graft, which shows that optimum concentration of PPy for grafting is 0.3 M.

Table 1
Percentage of grafting with pyrrole concentration and conductivity of sample.

Sample code	Concentration of pyrrole (M)	% of grafting	Conductivity S/cm
Chitin	–	–	$\approx 10^{-9}$
CP1	0.1	7	4.18×10^{-7}
CP3	0.3	46	7.87×10^{-7}
CP5	0.5	138	2.86×10^{-7}
PPy	–	–	2.64×10^{-8}

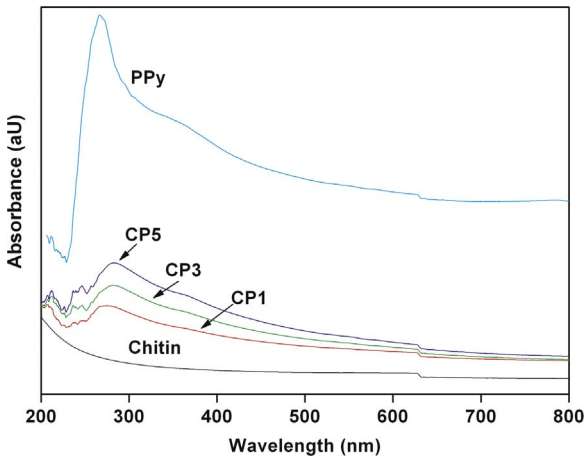

Fig. 3. UV–Vis spectra of graft polymers.

3.1. UV–Vis absorption spectra

The UV–Vis absorption spectra of chitin-PPy graft solutions are shown in the Fig. 3, an absorption edge is observed at ≈350 nm in all the grafted samples. Since there is no significant absorption peak or edge for chitin in this region, the absorption edge at ≈350 nm similar to the absorption edge observed for PPy, corresponds to π-π^* electron transition of pyrrole in the grafted samples [14–16]. Absorption bands corresponding to polarons (685 nm) or bipolarons (978 nm) [14–16] are not observed in the grafted samples.

3.2. XRD analysis

The effect of grafting on the molecular order of prepared grafted samples has been carried out by XRD analysis. The XRD patterns of grafted samples are shown in Fig. 4. PPy is associated with a broad

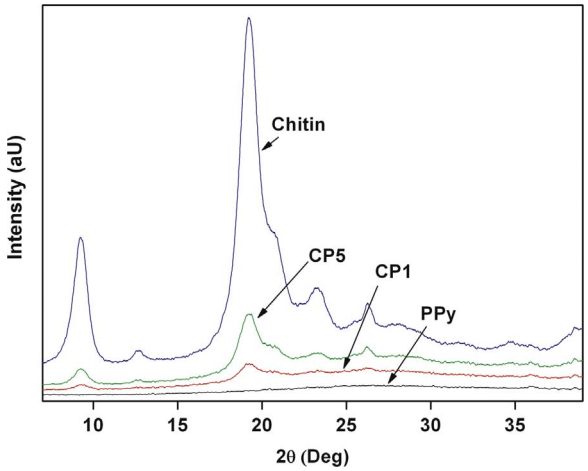

Fig. 4. XRD pattern of chitin-PPy grafted polymers.