

Sol-Gel Fabrication of Polyimide-Silica Hybrid Film and its Characterization through TGA and FTIR

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Received: 24 December 2019

Accepted: 07 February 2020

Published: 01 March 2020

Abstract

Polyimide-Silica hybrid films with nanostructure were successfully prepared using the sol-gel technique by hydrolysis-polycondensation of tetraethoxysilane (TEOS) in the polyamic acid solution. At the first step polyamic acid was prepared from 4,4 ((Hexafluoroisopropylidene) bis (phthalic anhydride) and Bis (4-aminophenyl) ether (ODA) in methanol/water (1:1 by volume) solution and a amber-colored product for the use in the polyimide synthesis was obtained. The sol-gel reaction requires water to hydrolyze tetraethoxysilane (TEOS), however the existence of water might induce the hydrolyze of polyamic acid , so a solution of polyamic acid in DMAc was stirred in the presence of 1ml of water to avoid the hydrolysis degradation of polyamic acid during the reaction. By heating at 270 °C flexible hybrid films were obtained containing up to 70% silica content. The films with less than 22% silica content were yellow and transparent, whereas the films with higher silica content were yellow and opaque. Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) were used to study hybrids containing various proportions of TEOS. Silica particles with diameter of around 60-105 nm were observed in hybrids films by scanning electron microscopy. The particale size increased with increasing the silica content. Thermogravimetric analysis (TGA) were done under N₂ atmosphere at a rate of 20°C/min.

Keywords: Sol-gel Process; Polyimide; Silica; Nanocomposite; Organicinorganic Hybrid Materials; Tetraethoxysilane.

How to cite the article:

Osman Al Maghrebi, Sol-Gel Fabrication of Polyimide-Silica Hybrid Film and its Characterization through TGA and FTIR, Medbiotech J. 2020; 4(1): 027-029, DOI: 10.22034/mbt.2020.105884.

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1. Introduction

Organic-inorganic composite materials are increasingly important due to their extraordinary properties, which arises from the synergism between the properties of the components. These materials have gained much interest due to the remarkable changes in their properties such as electrical, magnetic, optical transparency, mechanical and thermal, compared to pure organic polymers [1-4]. The most commonly employed preparation procedures for these materials are sol-gel process for the formation of the inorganic network. The sol-gel process, as the name implies,

involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel) [5]. Properties of a particular sol-gel inorganic network are related to a number of factors such as pH, temperature, time of reaction, reagent concentration, catalyst nature and concentration, water to alkoxy and catalyst to alkoxy ratios and the type of solvent [6]. Of the factors listed above pH, catalyst, temperature and the water to alkoxy and catalyst to alkoxy ratios have been identified as the most important ones. Most of the efforts are based on well-known macro

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or microcomposites between organic polymers and inorganic moieties, and expand ideas from this microcosmos to a new class of materials, called nanocomposites (NC) [7]. Important aspects of the chemistry involved in the formation of these systems are the uniformity, domain sizes, phase continuity and the molecular mixing at the phase boundaries, which have a direct influence on the optical, physical, and mechanical properties. Additionally, the properties of nanocomposites depend on the morphology of the phases, which has to be controlled over several length scales.

In this study, a novel system for preparation polyimide-silica hybrid films with silica particles at a nanometer scale was established and being discussed.

2. Experimental

2.1. Preparation of Polyamic Acid 3.

At first polyamic acid was prepared by adding 2 g (4.5×10^{-3} mol) 4,4'-(Hexafluoroisopropylidene)-bis-(phthalic anhydride) **1** and 0.9 g (4.5×10^{-3} mol) bis(4-aminophenyl)ether **2** in 15ml N,N-dimethylacetamide (DMAc) as the solvent into a round-bottomed flask equipped with a stirring magnet. The solution was stirred for 24 h at 0 °C. The resulting viscous polyamic solution was poured into 60 ml of methanol/water (1:1 v/v) solution. The precipitated polymer was filtered off and dried at 80 °C for 10 h under vacuum to give 2.9 g (100% yeild) amber-colored product as the precursor in polyimide-silica synthesis. IR : 3444 (s), 3049 (sh), 2937 (m, sh), 2484 (w), 1955 (w, br), 1784 (w, sh), 1731 (s), 1631 (s), 1545 (m), 1498 (s), 1402 (s), 1255 (s), 1211 (s), 1178 (s), 1070 (m), 1014 (m), 962 (m), 831 (m, sh), 719 (m, sh), 594 (m), 513 (w), 472 (w) cm^{-1} .

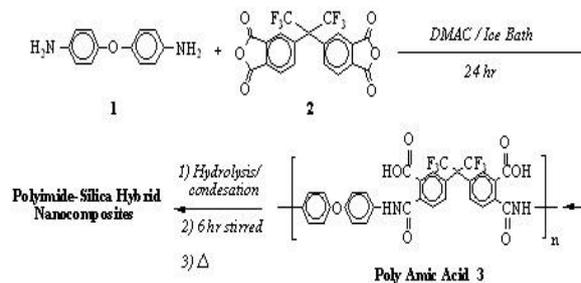
2.2. Preparation of the Polyimide-Silica Hybrid Films.

The desired amount of tetraethoxysilane (TEOS) and 0.03 ml water were added to 0.3 g of 10% wt solution of polyamic acid in DMAc in a round-bottomed flask. The mixture was stirred for 6 h until the heterogeneous solution became homogeneous. The film was formed by casting the solution on a glass plate. After being dried at 60 °C for 12 h, the resulting film was heated at 270 °C for 3h under N_2 . Formation of polyimide-silica hybrid film was confirmed by means of FT-IR spectroscopy.

3. Result and discussion

3.1. Polycondensation reaction

Polyimide-silica hybrid films were prepared by the two-step procedure as shown in Scheme 1.



Scheme 1

Polyamic acid **3** was prepared by solution polycondensation reaction of an equimolar amount of 4,4'-(Hexafluoroisopropylidene)-bis-(phthalic anhydride) **1** and bis(4-aminophenyl)ether **2** in DMAc. The product of this step was isolated by pouring of the reaction mixture into methanol/water (1:1 V/V). The precipitated amber-colored poly amic acid was filtered off and dried at 80 °C for 10 h under vacuum. The resulting polyamic acid was entered into the next step through the reaction with different amounts of TEOS to produce corresponding polymeric nanocomposite.

3.2. Polymer Characterization.

Chemical structure of the polyamic acid **3** was confirmed by means of FTIR spectroscopy.. A broad peak appeared at 2660-3800 cm^{-1} is related to the presence of COOH groups and two absorption bands at 1631 and 1731 cm^{-1} are characteristic peaks of amidic and acidic carbonyl groups respectively (NC1). Disappearance of the strong acidic hydroxyl peak in NC2-NC10 confirms the formation of desired polyimide. All of the spectra exhibited the strong absorbance at 1388 (C-N stretching) and 723 cm^{-1} (imide ring deformation), which shows the presence of the imidic heterocycle in these polymers. The absorption bonds in the range of 3116-3643 and 979 cm^{-1} are characterized as vibrational stretching of (Si-OH) and Si-O groups respectively that are formed during the hydrolysis of alkoxy groups in the presence of TEOS.

The scanning electron micrographs (SEM) of the fractured surface of the hybrid films give important information about the morphology of the hybrid materials. The dispersed silica particles could be seen as white spots with the diameter of 60-105 nm. The particle size increases with increasing the silica content. In spite of the particle size increasing as mentioned above all of the obtained polyimidesilica hybrids have retained their nanoscale structure.

3.3. Thermal Analysis.

TGA thermograms of hybrid nanocomposites under nitrogen atmosphere have been shown in Figure 1. A standard line shape analysis with multiple Gaussian fitting functions reveals that the

differential weight loss (DTG) curves of hybrids above 550 °C can be fitted by two degraded steps (Figure 2). The peak temperatures of each stage degradation in hybrid films are about 332-359.2 °C (T_{1m}) and 598-608 °C (T_{2m}) respectively, attributed to the scissions of siloxane and imide segments. These results suggest that the thermal stability of hybrid films has direct relationship with silica content.

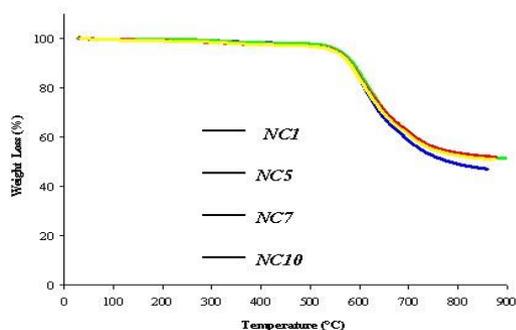


Figure 1 TGA thermograms of polyimide-silica nanocomposites: (NC1); 0, (NC5); 22, (NC7); 46 and (NC10); 70 wt % of silica content in N₂ at the heating rate of 20 °C/min.

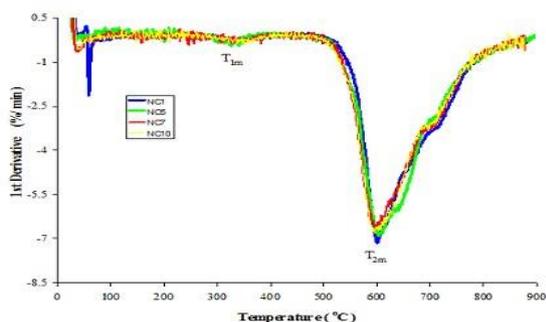


Figure 2 .DTG thermograms of polyimide-silica nanocomposites: (NC1); 0, (NC5); 22, (NC7); 46 and (NC10); 70 wt % of silica content in N₂ at the heating rate of 20 °C/min.

4. Conclusion

In conclusion, polyimide-silica hybrid films which were fairly flexible even in the case of 70 wt % of silica content were successfully prepared by the sol-gel process. Various proportions of TEOS were used. The incorporation of nanoscale inorganic species in organic polymers offers the possibility of the formation of a plethora of novel materials with a high potential for new application.

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