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Microwave-assisted synthesis of SiO₂ nanoparticles and its application on the flame retardancy of poly styrene and poly carbonate nanocomposites

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Abstract

Various morphologies of silica nanoparticles were synthesized by a microwave-assisted Pechini method. Silica nanostructures were synthesized via a fast reaction between tetra ethyl ortho silicate and ammonia at presence citric acid and other effective agents in Pechini procedure. Then for preparation of polymer-matrix nanocomposites, SiO₂ nanoparticles were added to poly carbonate (PC) and poly styrene (PS) matrices. Nanostructures were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR). The influence of SiO₂ nanostructures on the flame retardancy of the polymeric matrix was studied using UL-94 analysis. Our results show that the SiO₂ nanostructure can enhance the flame retardant property of the poly carbonate matrix. PC shows better flame retardancy compare to poly styrene.

1. Introduction

The microwave heating involves two main mechanisms, dipolar polarization and ionic conduction. Microwaves generally heat any material containing mobile electric charges such as polar molecules or conducting ions in a solvent or in a solid. During the microwave heating, polar molecules like glycol molecules try to orientate with the rapidly changing alternating electric field; thus heat is generated by the rotation, friction, and collision of molecules. In the case of ions, any ions present in solution will move through the solution based on the orientation of the electric field, and because this is in constant fluctuation, the ion is moving in constantly changing directions through the solution, causing a local temperature rise due to friction and collision. Semiconducting and conducting samples heat when ions or electrons within them form an electric current and energy is lost due to the electrical resistance of the material [1].

Important advantages of polymeric compounds over many metal compounds are high toughness, corrosion resistance, low density and thermal

insulation. Scientists for improvement the properties of composite materials investigate composites with nanofillers, leading to the development of nanocomposites. Improvement the fire retardant behavior of polymers is a major challenge for extending their use for most applications. Various flame retardant additives such as halogenated compounds are limited with respect to the environmental requirements [2–5]. One of the main drawbacks of traditional bulk additives is that for pass flame retardancy tests, 35 to 65 wt% of additives is required. Increasing the loading of inorganic fillers will result in a significant decrease in physical properties. The higher level of flame retardancy of nanoparticles is due to their bigger surface to volume fractions which let them to disperse into the polymeric matrix homogeneously, and hence leads to formation of a compact char during the combustion. Poly styrene and poly carbonate are commercial material with low cost and good mechanical properties. They are widely used as an important engineering thermoplastic polymer because of their desirable properties; which include suitable mechanical properties, chemical resistance and easy processing. One of the main disadvantages of the poly styrene is its inherent flammability; therefore there is a need to increase its thermal stability [6-10].

During the past few years, a variety of synthesis strategies for silica nanostructure materials have been described. Recently, microwave method as a simple, effective and novel route has been developed to prepare nanostructures. Microwave method is one of the fastest methods operated under ambient conditions [11-14].

In the last two decades polymer matrix nanocomposites have also been extensively investigated, since just a small amount of nanoparticles as an additive leads to production of novel high-performance materials with excellent physicochemical properties [15-19]. In this work, various morphologies of silica nanoparticles were synthesized by microwave-assisted Pechini method. Then for preparation of polymer-matrix nanocomposites, SiO_2 nanoparticles were added to poly carbonate (PC) and poly styrene (PS) matrices. PC shows better flame retardancy compare to poly styrene.

2. Experimental
2.1. Materials and characterization

Citric acid, oxalic acid, succinic acid, maleic acid and NH_3 were purchased from Merck Company. All the chemicals were used as received without further purifications. X-ray diffraction (XRD) patterns were recorded by a Philips X-ray diffractometer using Ni-filtered CuK_α radiation. A multiwave ultrasonic generator (Bandeline MS 73) equipped with a converter/transducer and titanium oscillator operating at 20 kHz with a maximum power output of 100 W was used for the ultrasonic irradiation. Scanning electron microscopy (SEM) images were obtained using a LEO instrument (Model 1455VP). Prior to taking images, the samples were coated by a very thin layer of Pt (BAL-TEC SCD 005 sputter coater) to make the sample surface conducting obtain better contrast and prevent charge accumulation.

2.2. Synthesis of SiO_2 nanoparticles

Firstly 22mmol of succinic acid (or citric acid, maleic acid or oxalic acid) was dissolved to the ethylene glycol. Then tetra ethyl ortho silicate (5mL), was dissolved in 15 mL of ethylene glycol. Then NH_3 solution was then slowly added to the mentioned solution (pH was adjusted about 9) under microwave radiation (600W , 5s On, 5s Off) for 2 minutes. The white precipitate is then centrifuged and rinsed with distilled water and left in 100 ℃ to

dry. The product was calcined at 400ºC for 2h. Schematic of various capping agents that were used in Pechini method is given in Fig. 1.

For synthesis of nanocomposite, 5g of poly styrene (or poly carbonate) was first dissolved in dichloromethane (10 mL). The SiO_2 nanoparticles (1 g) were dispersed in dichloromethane (5 mL) by ultrasonic waves. The nanoparticles dispersion is then slowly added to the polymer solution. The new solution is then stirred for 6 hours. To evaporate the solvent, the product is casted on a glass plate and left for 48 hours Fig. 2.
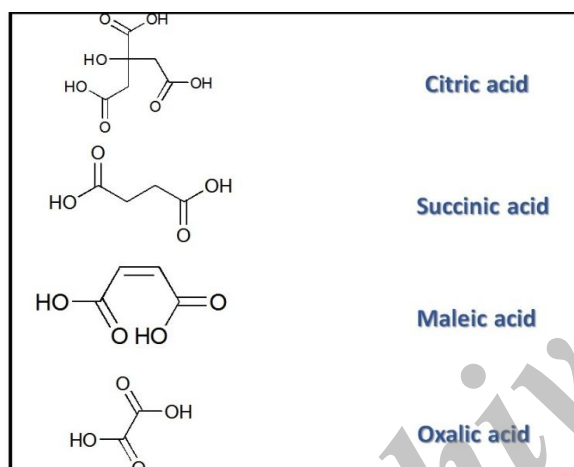
Fig. 1. Schematic of various capping agents

3. Results and discussion

The XRD pattern of SiO_2 nanoparticles is shown in Fig. 3 and is indexed as a tetragonal phase (space group: 1-42b). The experimental values are very close to the literature (JCPDS No. 47-0715). The crystallite size measurements were carried out using the Scherrer equation (Eq. 1),

$$Dc=0.9\lambda/\beta\cos\theta \qquad (1)$$

where β is the width at half maximum intensity of the observed diffraction peak, and λ is the X-ray

wavelength (CuK_α radiation, 0.154 nm). The estimated crystallite size is about 10 nm.

Based on our literature search, there are few reports on effect of SiO_2 on flame retardancy of poly styrene and poly carbonate nanocomposites. Therefore, we studied the SiO_2 interaction between the nanoparticles surrounded by poly styrene and polycarbonate chains.
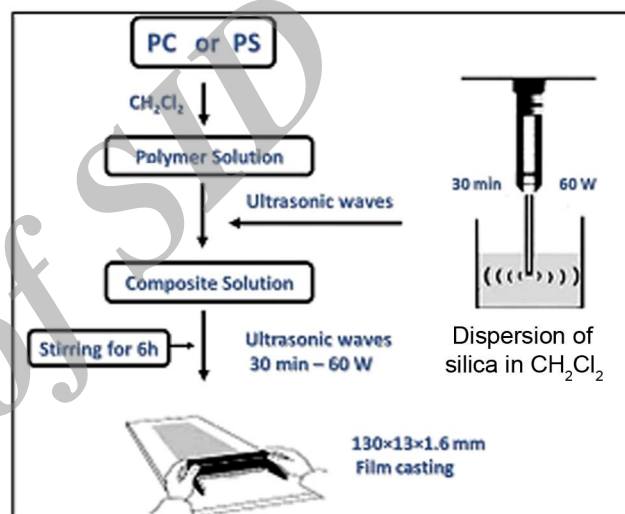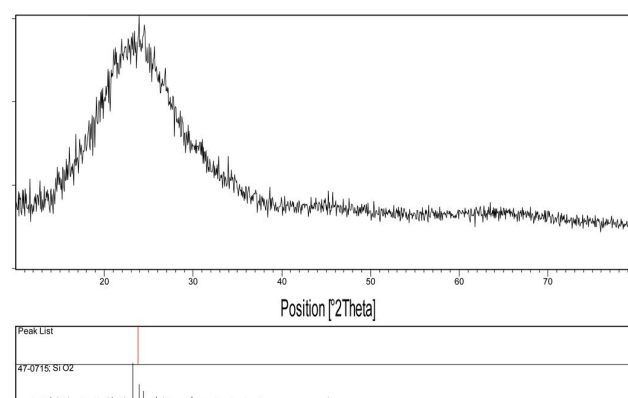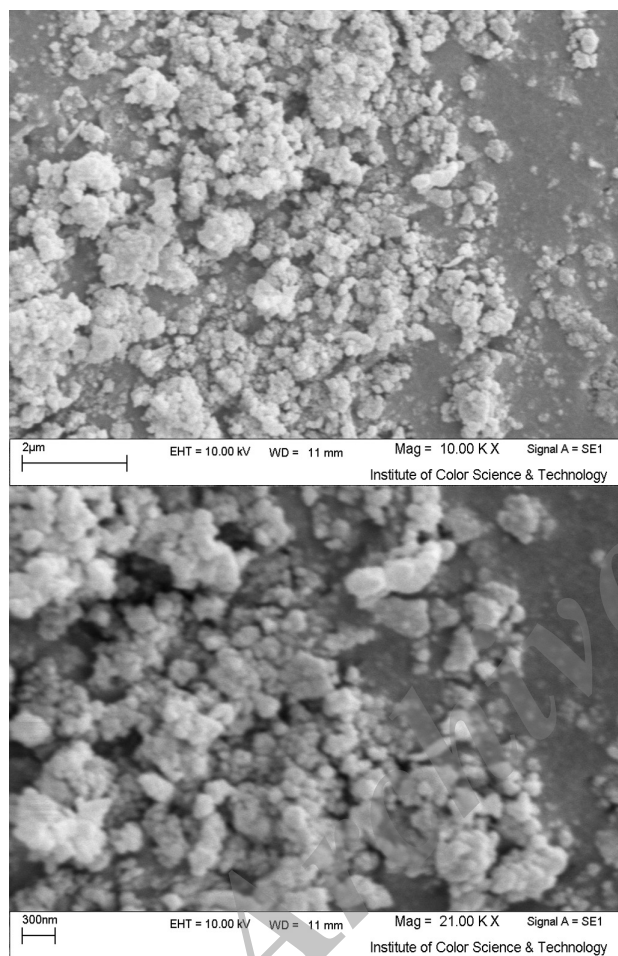

Fig. 2. Schematic of nanocomposite preparation

Fig. 3. XRD pattern of SiO_2 nanoparticles

SiO_2 has barrier effect to slow down the product volatilization and thermal transport during decomposition of the polymer.
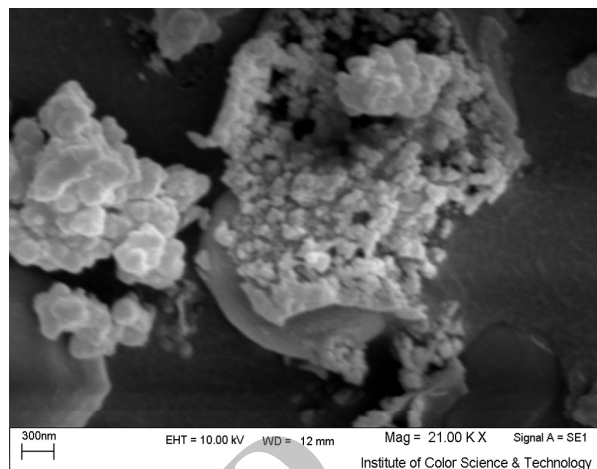
Scanning electron microscopic images of SiO_2 nanoparticles achieved by citric acid are illustrated in **Fig. 4**. Nanoparticles with average diameter about 80 nm were synthesized. Citric acid has a suitable interaction with ethylene glycol in formation of sol-gel procedure in preparation of nanostructures.


Fig. 5. SEM image of nanoparticles synthesized by maleic acid

Fig. 4. SEM images of SiO_2 nanoparticles achieved by citric acid

Fig. 5 depicts SEM image of nanoparticles synthesized by maleic acid. The agglomeration was observed and it seems growth stage overcomes to nucleation stage and bigger particles were synthesized.

SEM images of SiO_2 obtained by succinic acid are shown in **Fig. 6.** Nanoparticles with mediocre diameter size about 70 nm were obtained.
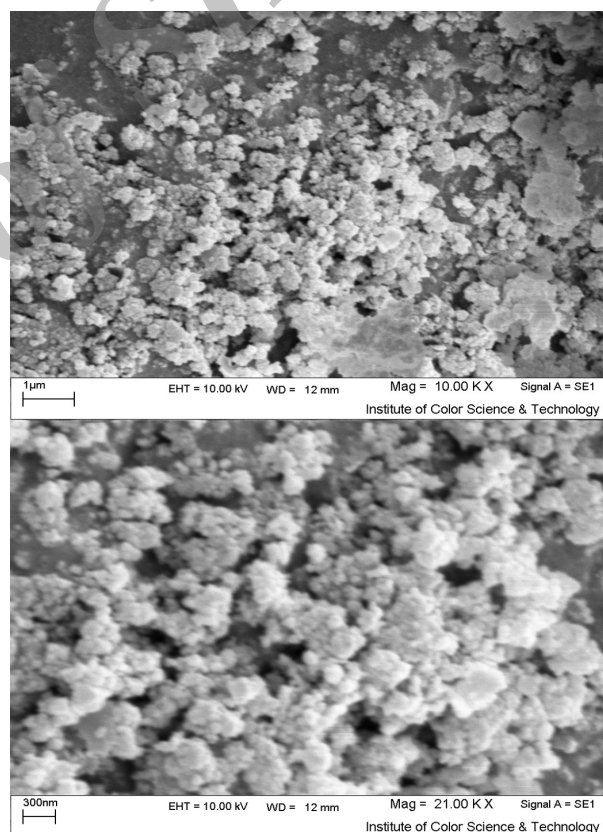
Fig. 6. SEM images of SiO_2 obtained by succinic acid

Fig. 7 shows SEM images of SiO_2 synthesized by oleic acid. Preferential growth was observed and as a result flower-like nanostructures were synthesized. Nanostructures were formed from nanoparticles with average particle size less than 20 nm.

FT-IR spectrum of SiO$_2$ nanoparticles is illustrated in Fig 8. Absorption peak around 1091 cm^{-1} is related to Si-O bonds. The spectrum exhibits broad absorption peaks between 3500-3600 cm^{-1}, corresponding to the hydroxyl group that are adsorbed on the surface of nanoparticles

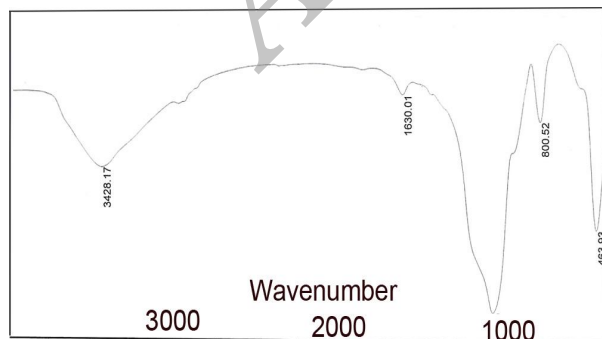**Fig. 7.** SEM images of SiO$_2$ synthesized by oleic acid

Fig. 8. FTIR spectrum of SiO$_2$ nanoparticles

The effect of nanostructure on the flame retardant properties has been considered using UL-94 test. In UL-94 a bar shape specimen of plastic $130 \times 13 \times 1.6$ mm is positioned vertically and held from the top. A Bunsen burner flame is applied to the specimen twice (10 s each). A V-0 classification is given to material that is extinguished in less than 10 s after any flame application, drips of particles allowed as long as they are not inflamed. A V-1 classification is received by a sample with maximum combustion time < 30 s, drips of particles allowed as long as they are not inflamed.
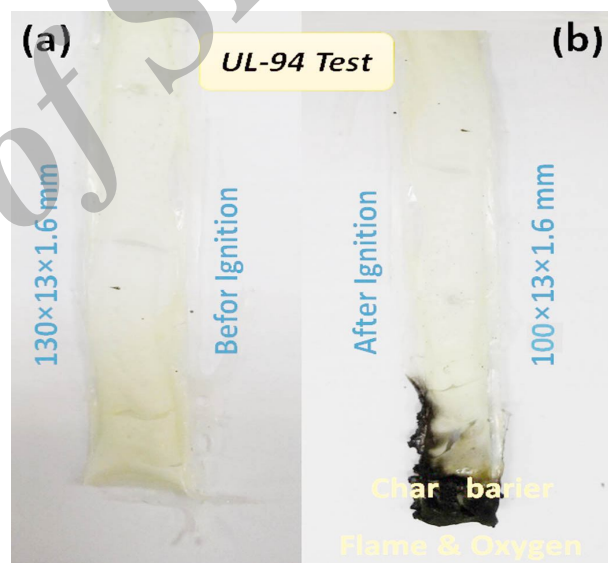

Fig. 9. UL94 of pure PS (a) before (b) after ignition

The sample is classified V-2 if it satisfies the combustion time criteria of V-1, but flaming drips are allowed. Materials are ranked as N.C. in UL-94 tests when the maximum total flaming time is above 50 s.

The results of UL-94 tests for poly styrene and poly styrene/SiO$_2$ nanocomposites are N.C and V-2 respectively (Fig. 9). The outcomes show that the SiO$_2$ nanostructure can enhance slightly flame retardant property of the poly styrene matrix. The

results of UL-94 tests for poly carbonate and poly carbonate/SiO_2 nanocomposites are N.C and V-0 respectively (Fig. 10). The test shows that the SiO_2 nanostructure can improve flame retardancy of the poly carbonate matrix. The enhancement of flame retardancy of nanocomposite is due to suitable interaction between mono-disperse silica nano-filler and poly carbonate matrix. The increase of flame retardancy of nanocomposite is because of barrier effect to slow down the product volatilization and thermal transport during decomposition of the polymer.
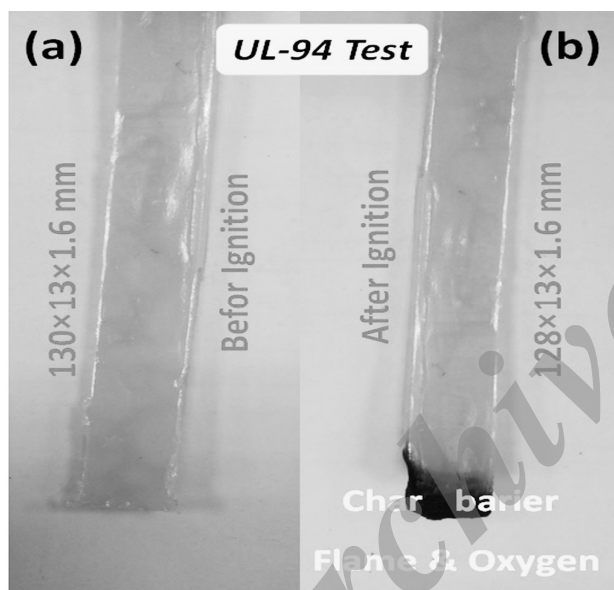

Fig. 10. UL94 of pure PC (a) before (b) after ignition

4. Conclusion

SiO_2 nanoparticles were prepared by a simple microwave-assisted Pechini process. SiO_2 nanoparticles were then added to poly styrene and poly carbonate matrices. The influence of the inorganic phase on the thermal properties and flame retardancy of poly styrene and poly carbonate matrices was studied. The results show that the SiO_2 can enhance the flame retardant property of the poly carbonate matrix. The enhancement of flame retardancy of

nanocomposite is because of insulation effect to slow down the product volatilization and thermal transport during decomposition of the polymer.

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