RESEARCH PAPER

Hydrothermal Synthesis of Fe_3O_4 Nanoparticles and Flame Resistance Magnetic Poly styrene Nanocomposite

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ARTICLE INFO

Article History:
Received 02 October 2016
Accepted 12 November 2016
Published 01 January 2017

Keywords:
Flame Retardancy
Magnetic
Nanocomposite
Nanoparticles

ABSTRACT

Fe_3O_4 nanostructures were synthesized via a facile hydrothermal reaction. The effect of various surfactants such as cationic and anionic on the morphology of the product was investigated. Magnetic nanoparticles were added to poly styrene for preparation of magnetic nanocomposite. Nanostructures were then characterized using X-ray diffraction, scanning electron microscopy and Fourier transform infrared spectroscopy. The magnetic properties of the samples were also investigated using vibrating sample magnetometer. The magnesium ferrite nanoparticles exhibit super paramagnetic behaviour at room temperature, with a saturation magnetization of 66 emu/g and a coercivity less than 5 Oe. Distribution of the magnetic nanoparticles into poly styrene matrix increases the coercivity. Nanoparticles appropriately enhanced flame retardant property of the PS matrix. Nanoparticles act as barriers which decrease thermal transport and volatilization during decomposition of the polymer.

How to cite this article
Hedayati K, Goodarzi M , Ghanbari D. Hydrothermal Synthesis of Fe_3O_4 Nanoparticles and Flame Resistance Magnetic Poly styrene Nanocomposite. J Nanostruct, 2017; 7(1):32-39. DOI: 10.22052/jns.2017.01.004

INTRODUCTION

Magnetite nanostructures are used in various strategic devices and have applications in industrial and medical equipments. Magnetite is one of the important member of Ferrites that show great technological and scientific interest considering their physical properties such as appropriate magnetization, high coercivity, chemical stability and cost effectiveness. The interest in them has grown enormously, and is still growing today. The ferrite materials may be classified into three different classes; spinel ferrites, garnet ferrites and hexagonal ferrites [1-4]. Preparation of Fe_3O_4 nanostructures is important for its novel magnetic properties, particularly super-paramagnetic behavior, and biomedical applications. The ecofriendly ferrites are well known for their enormous applications in the field of magnetic and electronic materials and photocatalytic applications.. The ferrites were used for magnetic recording, data storage materials, radar absorbing materials due to their strong magnetic losses at the range of GHz frequency, magnetoelectric/multiferroic applications [5-11].

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.

Polystyrene is one of the most famous thermoplastic polymers and is widely applicable plastics and its production being several million tonnes

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each year. Polystyrene is naturally transparent while it can be colored with colorants. Uses include protective packaging containers bottles, trays, tumblers and disposable cutlery [11-13].

Polystyrene is in a solid (glassy) state at room temperature but flows if heated above about 100 °C, its glass transition temperature. It becomes rigid again when cooled. This temperature behavior is exploited for extrusion and also for molding and vacuum forming, since it can be cast into molds with fine detail [14,15]. In this work, we report synthesis of Fe_3O_4 using hydrothermal reaction. The Fe_3O_4 nanoparticles were then incorporated in poly styrene. Magnetic properties of Fe_3O_4 nanoparticles and nanocomposites were also compared. Nanoparticles also appropriately enhanced flame retardant property of the PS matrix.

MATERIALS AND METHODS

$Fe(NO_3)_3$ $9H_2O$, $FeCl_2$ $4H_2O$ and dichloromethane were purchased from Merck Company. All the chemicals were used as received without further purifications. XRD patterns were recorded by a Philips, X-ray diffractometer using Ni-filtered CuK_α radiation. A multiwave ultrasonic generator (Bandeline MS 72), 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. SEM images were obtained using a LEO instrument model 1455VP. Prior to taking images, the samples were coated by a very thin layer of Au (using a BAL-TEC SCD 005 sputter coater) to make the sample surface conductor and prevent charge accumulation, and obtaining a better contrast. Room temperature magnetic properties were investigated using a vibrating sample magnetometer (VSM) device, made by Meghnatis Daghigh Kavir Company (Iran) in an applied magnetic field sweeping between ±10000 Oe. In UL-94 a bar shape sample 130 × 13 × 1.6 mm is held vertically. A Bunsen burner flame is applied to the specimen twice (10 s each).

Synthesis of Fe_3O_4 nanoparticles

0.01 mol of $FeCl_2$ $4H_2O$, 0.02 mol of $Fe(NO_3)_3$

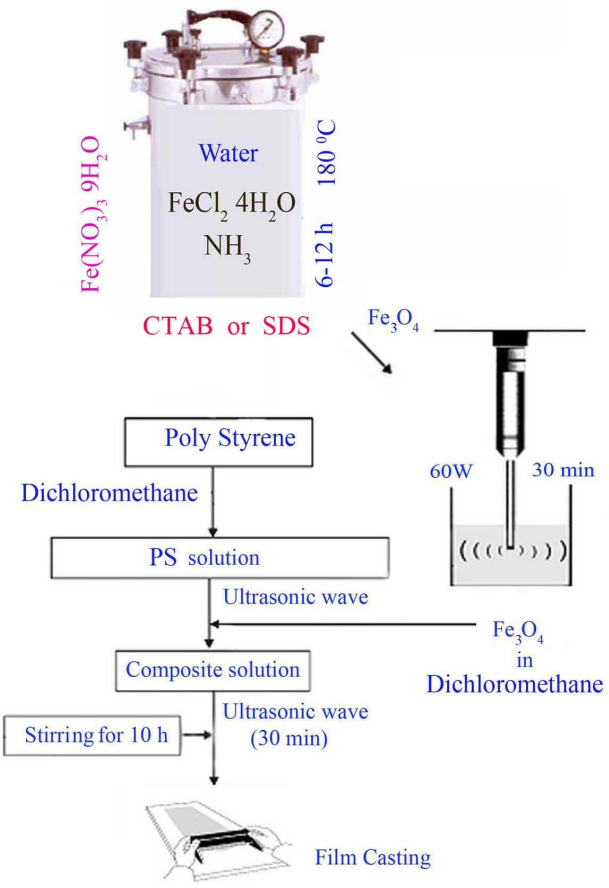

Fig. 1. Schematic of preparation of nanocomposite

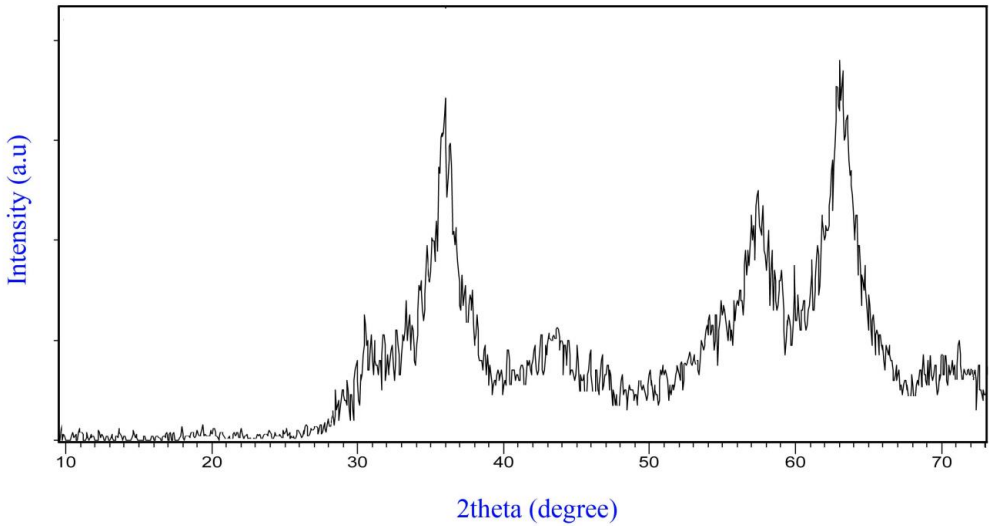

Fig. 2. XRD pattern of Fe_3O_4 nanoparticles

$9H_2O$ and 0.7g of surfactant (sodium dodecyl sulphate or cethyl tri-methyl ammonium bromide) were dissolved in 100 mL of distilled water. 10 mL of NH_3 solution 1 M was then slowly added to the solution. The reactants were then put into a Teflon-lined autoclave of 500 ml capacity. The autoclave was maintaining at 200 °C for 4 h. The black magnetic product was centrifuged, washed with distilled water and dried in the air.

Preparation of nanocomposite

4 g of poly styrene was dissolved in 15 ml dichloromethane solution. 1 g of nanoparticles Fe_3O_4 was dispersed in 10 ml dichloromethane solution with ultrasonic waves (30 min, 100W). Then nanoparticles dispersion was slowly added to the polymer solution. The new solution was then mixed and stirred for 10 hours. In order to evaporate the solvent, the product was casted on a piece of glass template and it is left for 24 hours (Fig. 1).

RESULTS AND DISCUSSION

The XRD pattern of Fe_3O_4 nanoparticles is shown in Fig. 2. The XRD pattern of as-prepared Fe_3O_4 nanoparticles is indexed as a pure cubic phase (space group:Fd-3m) which is very close to the literature values (JCPDS No. 01-1111).

The crystallite size measurements were also carried out using the Scherrer equation,

$$Dc=K\lambda/\beta Cos\theta$$

Where β is the width of the observed diffraction peak at its half maximum intensity (FWHM), K is the so-called shape factor, which usually takes a value of about 0.9, and λ is the X-ray wavelength (CuK_α radiation, equals to 0.154 nm). The estimated crystallite size is about 15 nm.

Fig. 3 show Scanning Electron Microscopy images of the product that were prepared without applying surfactant, results confirm that nanoparticles with average particle size around 50 nm were observed. Images also depict some agglomeration was observed with mono-disperse product.

Fig. 4 show SEM images of the product when sodium dodecyl sulphate (SDS: anionic surfactant) was used that confirm mono-disperse nanoparticles with mediocre size around 30 nm were synthesized.

Also by using cethyl tri-methyl ammonium bromide (CTAB: cationic surfactant) nanoparticles with average diameter of 30 nm were obtained (Fig. 5). It show nucleation stage overcome to growth stage and therefore nanoparticles were achieved.

By using anionic surfactant growth stage has been preferred in comparison to nucleation stage and as a result the best mono-dispersion were achieved.

We have used hydrothermal method for this synthesis. Obviously hydrothermal is a unique method for fabricating nanostructures with specific and controlled morphologies. While predominant morphology in other methods like sol-gel, sonochemical and etc is nanoparticle. Hydrothermal method provides preferred

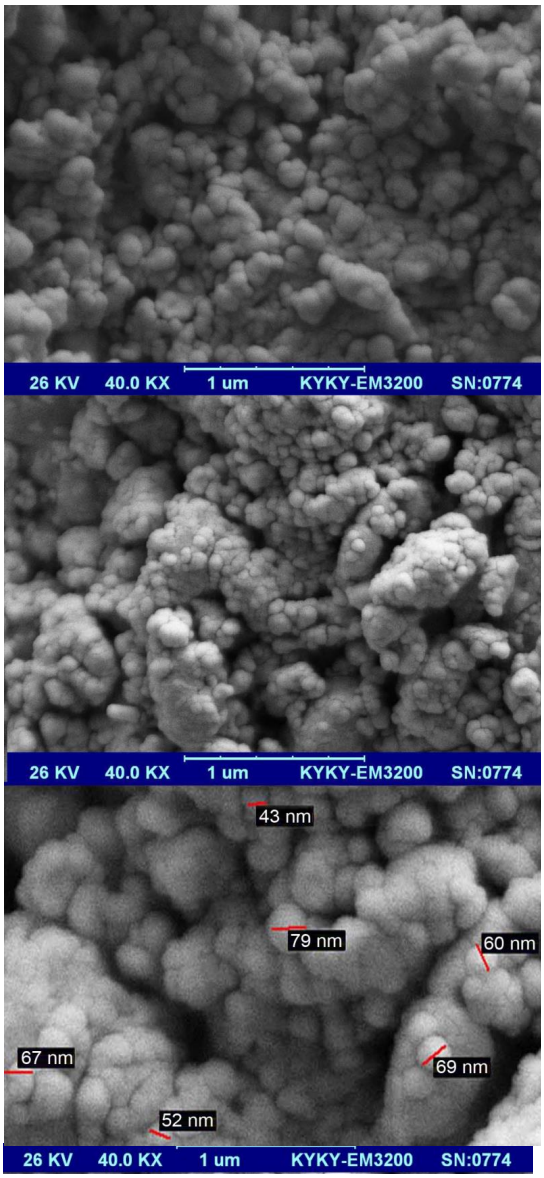

Fig. 3. SEM images of surfactant-free prepared nanostructures

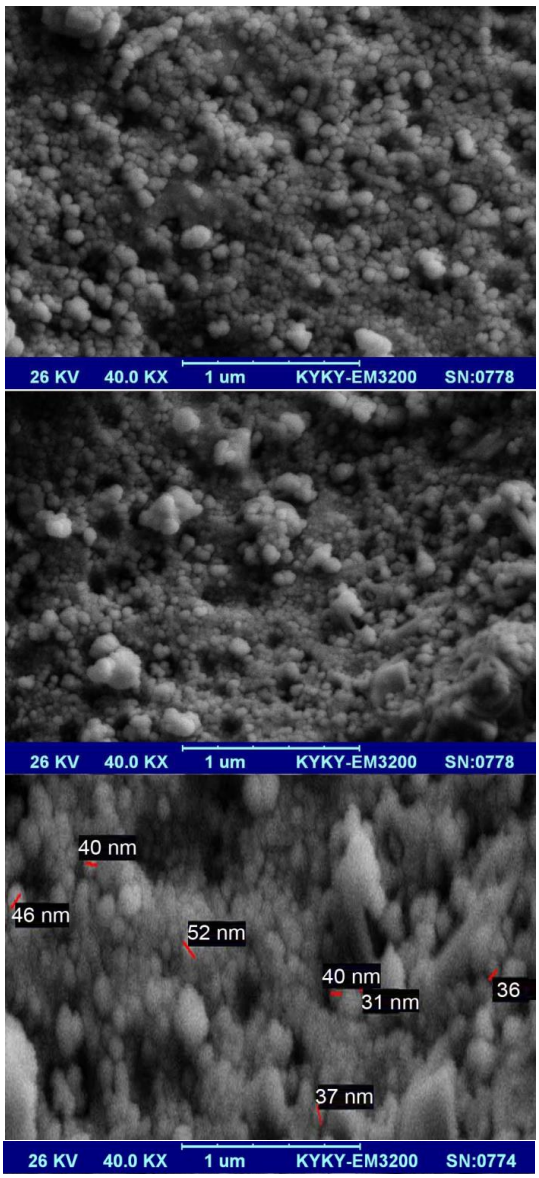

Fig. 4. SEM images of nanoparticles obtained by SDS

orientation morphology. In hydrothermal method because of some particular conditions (high temperature and pressure) the nanoparticles grow in situ and form nanostructure shape [1-3].

FT-IR spectrum of Fe_3O_4 nanoparticles is depicted in Fig. 6. Absorptions at 453 and 561 are related to Fe-O bonds in nanoparticles and absorption in 3430 is responsible to O-H that adsorbed on the surface of the nanoparticles. Fig. 7 is FT-IR spectrum of PS-Fe_3O_4 nanocomposite, an absorption peak occurs at 1450 cm^{-1} is related to the C=C bond in PS. Absorption at 2950 and 3050 cm^{-1} are referred to the stretching vibration of aliphatic and aromatic bonds. Absorption at 410 cm^{-1} at nanocomposite confirms existence of the Fe_3O_4 in the poly styrene matrix.

Room temperature magnetic properties of samples were studied using a vibrating sample magnetometer device. Hysteresis loop for Fe_3O_4 nanoparticles is shown in Fig. 8. It was found that the as-prepared Fe_3O_4 nanoparticles show a super paramagnetic behaviour with a saturation magnetization of 66 emu/g and a coercivity of 5 Oe at room temperature.

HysteresisloopforPS-$Fe_3O_4$90:10%nanocomposite is illustrated in Fig. 9. Fe_3O_4 nanostructures exhibit

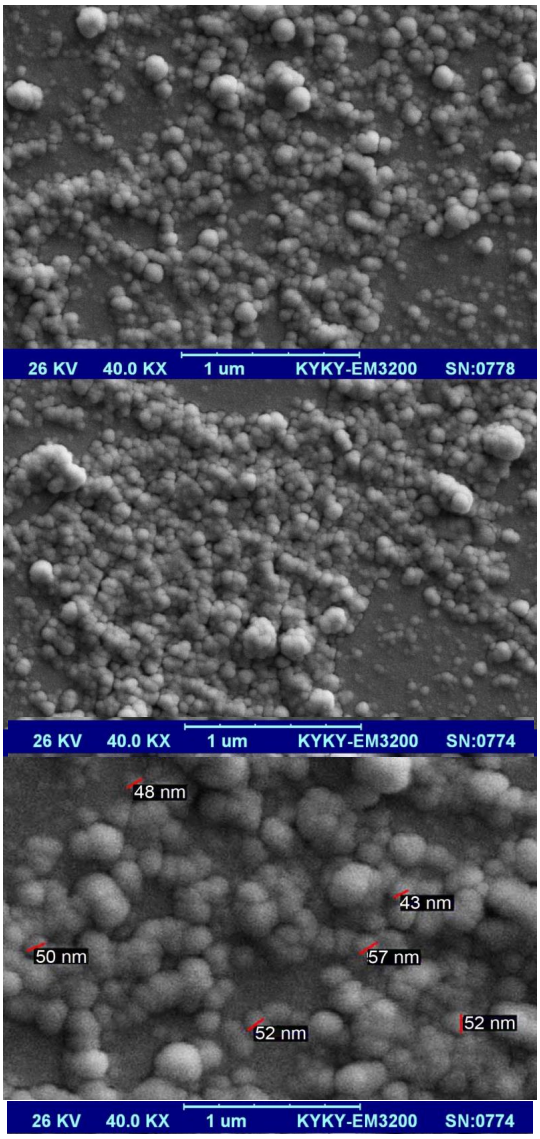

Fig. 5. SEM images of nanoparticles obtained by CTAB

a super paramagnetic behaviour with a saturation magnetization of 55 emu/g and a coercivity of 10 Oe at room temperature.

Hysteresis loop for PS-Fe_3O_4 50:50% nanocomposite is illustrated in Fig. 10. Nanocomposite exhibits a saturation magnetization of 29 emu/g and a coercivity of 20 Oe at room temperature.

In our best knowledge and based on our search in the literature very few work has been done on magnetic poly styrene nanocomposites. We studied the magnetic interaction between the nanoparticles surrounded by the polymeric chains. This interaction leads to an increase of nanoparticle coersivities compared with the pure magnesium ferrite nanoparticles.

For making 5g of magnetic nanocomposite, 1 g of ferrite nanoparticles was added to 4 g of polymer. Thus the nanocomposite magnetization (defined as the magnetic moment per unit volume) is about one fifth of which is obtained for Fe_3O_4 nanoparticles.

The saturation magnetization of Fe_3O_4 nanoparticles is higher than that is obtained for PS-Fe_3O_4 nanocomposites. Coercivity of magnetic nanocomposites highly depends on the magnetic nanoparticle distribution into the polymeric matrix.

The results also indicate that, forming the nanocomposite and dispersion of the magnetite in the polymer matrix leads to enhancement of the coercivity (from 5 to 20 Oe). The magnetic moments of magnetic nanoparticles are pined by the poly styrene matrix chains, so that a higher magnetic field is requires to align the single domain nanoparticles in the field direction

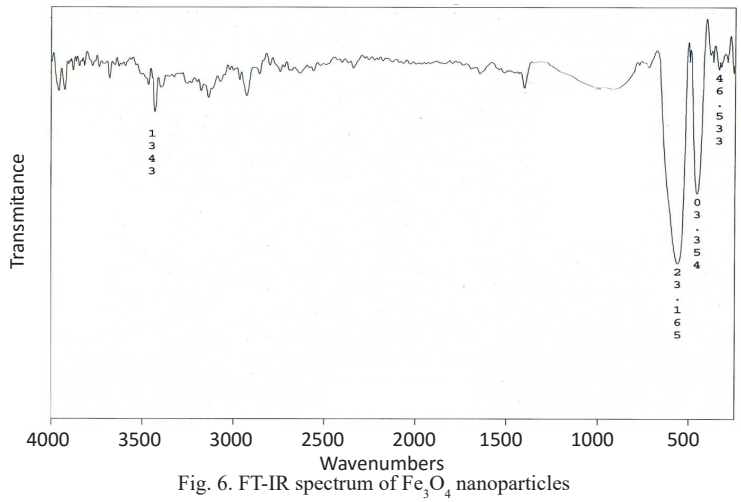

Fig. 6. FT-IR spectrum of Fe_3O_4 nanoparticles

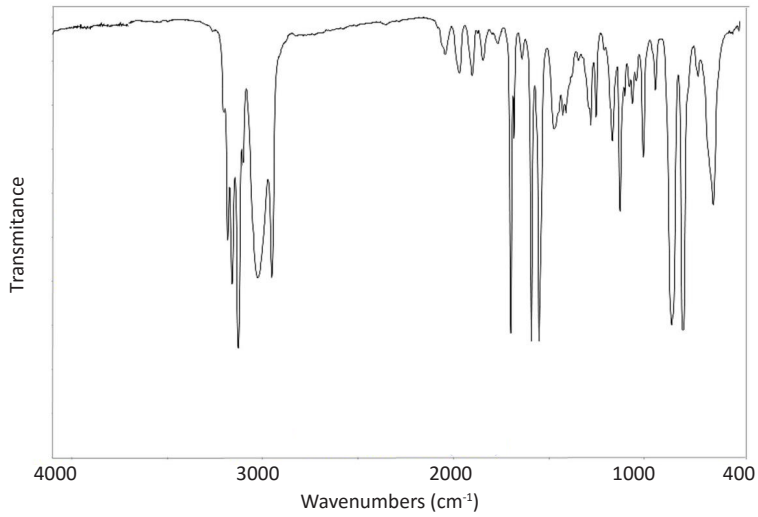

Fig. 7. FT-IR spectrum of PS-Fe_3O_4 nanocomposite

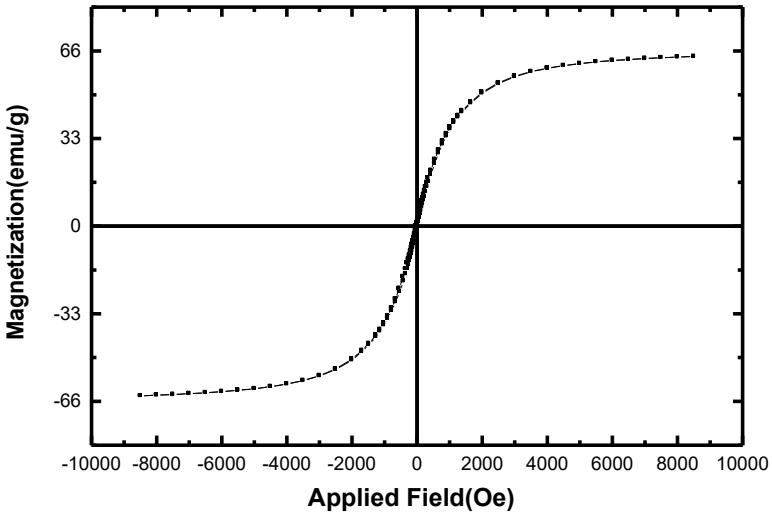

Fig. 8. Room temperature hysteresis loop of Fe_3O_4 nanoparticles

.The influence of Fe_3O_4 on the flame retardancy has been considered using UL-94 test. If sample extinguished in less than 10 second after any flame application classified as V-0, drips of particles were allowed as long as they are not inflamed.

A V-1 classification is given to by a sample with maximum combustion time less than 30 second, circumstances of drips are like V-0. The sample is classified V-2 if it has the combustion time criteria of V-1, but flaming drips are allowed. Samples are ranked as N.C. in UL-94 tests when the maximum total flaming time is above 50 s. The sample is classified HB when slow burning on a horizontal specimen; burning rate less than 76 mm/min [16-20].

The outcomes of UL-94 tests for PS and PS-Fe_3O_4 are N.C and V-0 respectively. The results show that the Fe_3O_4 can enhance the flame retardant property of the PS matrix. According to the UL-94 test, nanoparticles have been appropriately interacted to in PS matrix. Comparison of pure PS and PS-Fe_3O_4 nanocomposite under UL-94 test is shown in Fig. 11. Nanoparticles can play the role of a barrier magnetic layer; this barrier layer prevents heat or flame from reaching to the sample.

CONCLUSIONS

Fe_3O_4 nanostructures were synthesized via

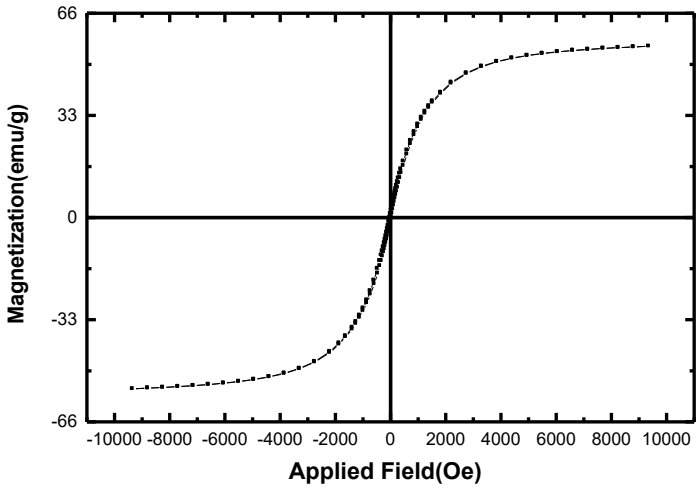

Fig. 9. Hysteresis loop of PS-Fe_3O_4 10:90 % nanocomposite

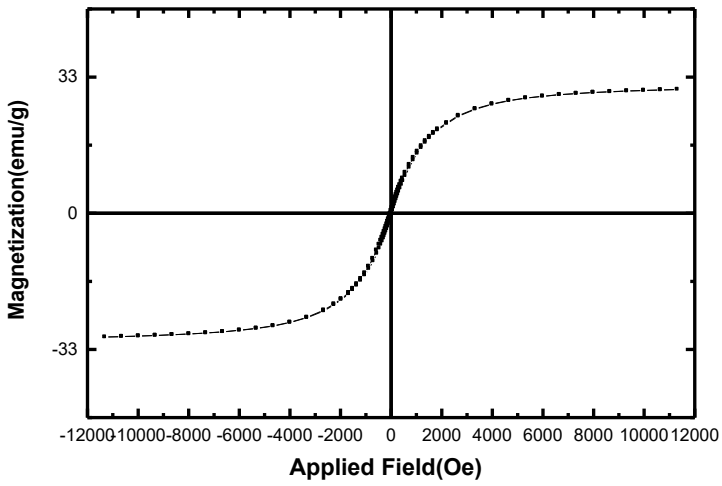

Fig. 10. Room temperature hysteresis loop of PS-Fe_3O_4 50:50 % nanocomposite

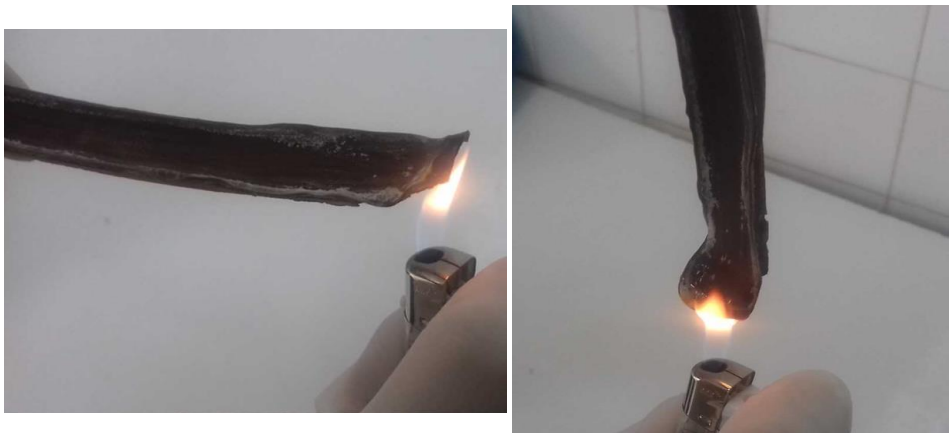

Fig. 11. PS-Fe_3O_4 nanocomposite under UL-94 test

a simple hydrothermal reaction. The effect of various surfactants such as cationic and anionic on the shape of the product was investigated. Fe_3O_4 nanoparticles exhibit a super paramagnetic behaviour with a saturation magnetization of 66 emu/g and a coercivity of 5 Oe at room temperature. Fe_3O_4 nanoparticles were then added to PS polymeric matrix in order to make magnetic nanocomposites. Distribution of the Fe_3O_4 nanoparticles into the polymeric matrix increases the coercivity. The results show that the Fe_3O_4 can enhance the flame retardant property of the PS matrix.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publicaton of this manuscript.

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