Synthesis, Characterization, Thermal Stability and Magnetic Properties of Nanocomposite Films of ABS and Iron Oxide Nanoparticles

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Abstract: Iron oxide nanoparticles (FNPs) synthesized by co-precipitation were used to prepare a nanocomposite with acrylonitrile-butadiene-styrene polymer (FNPs/ABS). The structure and particle size of the FNPs and FNPs/ABS nanocomposite were characterized by X-ray diffraction (XRD). The obtained nanopowders have a spherical structure and a particle size of approximately 3.5 nm as determined by transmission electron microscopy (TEM). The band gaps of the FNPs and FNP/ABS nanocomposite were estimated by UV-Vis spectroscopy. Vibrating sample magnetometry (VSM) was used to investigate the magnetic properties of the FNPs and FNPs/ABS nanocomposite. The FNPs and the FNPs/ABS nanocomposite were found to exhibit superparamagnetic behaviour: the coercivity (Hci) of the FNP/ABS nanocomposite (36.604 G) is higher than the coercivity of pure FNPs (24.810 G). Thermal stability testing showed that the residual weight percent of pure ABS after heating to 800°C was enhanced by adding 10% nanofiller.

Keywords: Co-precipitation, Iron oxide, ABS, Nanocomposite, Optical properties, Magnetic properties, Thermal stability.

Introduction

Magnetic nanomaterials have received much attention because of their desirable properties in technological applications, such as catalysis, magnetic storage, sensing, environmental protection, pharmaceuticals and cancer treatment[1-5].

In nature, iron oxide has many forms, including magnetite (Fe$_3$O$_4$), maghemite ($\gamma$-Fe$_2$O$_3$) and hematite ($\alpha$-Fe$_2$O$_3$). The physical and chemical properties of iron oxide nanoparticles vary with both their atomic and bulk compositions. Fe$_2$O$_3$ nanoparticles (NPs) are promising semiconductors for the study of both magnetic and structural phase transitions[4-6].

Acrylonitrile butadiene styrene (ABS) is a thermoplastic polymer with valuable thermal stability and mechanical properties. Nanofiller-strengthened polymer composites are often used in optical and magnetic devices and the behaviour of an ABS polymer can be tuned by the addition of different amounts of nanofillers[7].

Incorporation of magnetic nano-sized metal oxides into a conducting polymer matrix can lead to the production of materials that can be designed for many applications. Organic materials possessing a magnetic function have attracted interest due to their unique properties. These electromagnetic composites can be used for therapeutic or analytical purposes, such as drug release in the body[8]. Strengthening thermoplastic polymers with NPs to form nanocomposite is a method to expand the applications of polymeric materials by improving their properties, i.e., increase their mechanical properties with filler contents as low as 5–10 wt%. Moreover, the shape, size and ratio of the filler play essential roles in determining the morphological, optical and thermo-mechanical properties as well as the flame resistance of the nanocomposite[9].
M. C. Mascolo et al. synthesized magnetite NPs shows characteristics of superparamagnetism at room temperature, where the saturation magnetization (Ms) value depends on the crystal size and the degree of agglomeration of the NPs. In another study, the value of the room temperature saturation magnetization of composite samples of α-Fe₂O₃ and Co₃O₄ exhibited an increasing trend with increasing Co oxide content in the sample.

In this work, we report on the synthesis of iron oxide NPs and the mixing of these FNP with an ABS polymer to prepare an FNPs/ABS nanocomposite with 10% nanofiller. We studied the effect of the added FNP on the thermal properties of the ABS by thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). In addition, XRD, energy dispersive analysis X-ray (EDAX) and transition electron microscopy (TEM) were used to study the morphology of the FNPs. The optical properties were also studied by using UV-Vis spectroscopy to estimate the band gap of the FNPs and FNPs/ABS nanocomposite. Vibrating sample magnetometry (VSM) was used to characterize and detect changes in the magnetic properties of the ABS after adding the nanomagnetic filler to analyze the performance of the materials for different technological applications.

### Experimental Procedure

#### Materials and Methods

All reagents used in this investigation were of analytical grade and purchased from Sigma Aldrich, Co., Ltd. (USA). Iron(III) chloride hexahydrate (FeCl₃·6H₂O) and iron(II) chloride tetrahydrate (FeCl₂·4H₂O) were used as the iron precursors, sodium hydroxide (NaOH) was the precipitating agent and ethanol (C₂H₅OH) was used for washing. Acrylonitrile-butadiene-styrene (ABS) was obtained from SABIC (Saudi Arabia) and HPLC-grade dichloromethane was purchased from Fisher Chemical. All solutions were prepared with deoxygenated distilled water.

#### Synthesis of FNP Powders

Fe-oxide nanoparticles were synthesized by co-precipitation. In this procedure, an aqueous solution was prepared by dissolving 0.6 g of FeCl₃·6H₂O and 0.3 g of FeCl₂·4H₂O in 50 ml of deoxygenated distilled water separately. The solutions were mixed together at room temperature. Then, a 6 M NaOH solution was added dropwise as the precipitating agent to maintain a pH value of 11. The reaction vessel was heated to 90°C under magnetic stirring for 1 hour. The obtained precipitate was washed several times and a dry black powder was obtained. Finally, the dry black powder was annealed at 400°C for 4 hours.

#### Preparation of FNP/ABS Nanocomposite Films

One gram of ABS was dissolved in 10 ml of dichloromethane and stirred for 30 minutes. A 10% FNPs/ABS nanocomposite was prepared by mixing appropriate amounts of calcined FNPs with the above solution. Then, the solution was cast at room temperature in a petri dish until it dried to form the FNP/ABS nanocomposite.

#### Characterization and Measurements

The sample structure was characterized by X-ray diffraction (XRD) using a Shimadzu 7000 Diffractometer operating with a Cu Kα source (λ = 0.15406 nm) with a scan rate of 2° min⁻¹ for 2θ values between 10° and 90°. The elemental composition was estimated by energy dispersive X-ray analysis (EDAX) with an accelerating voltage of 20.0 kV attached to a scanning electron microscope (SEM). Transmission electron microscopy (TEM) was performed on a JEOL JEM 3010 at 3 kV. The optical properties of the FNPs and FNPs/ABS nanocomposite were characterized by UV-Vis absorption from 200–800 nm (JASCO UV-Vis spectrophotometer, Model V-670, Japan Instrument). The thermal behaviour of the prepared samples was examined using a TGA Q500 (V20.13 Build 39) to study the thermal stability of the FNP/ABS nanocomposite. DSC curves were obtained using a TA Instruments Q1000 DSC (V9.9 Build 303). Vibrating sample magnetometry (VSM) was used to study the magnetic properties of the prepared samples for applications with weights up to 20 kg at room temperature.

### Results and Discussion

#### Characterization of FNPs and FNPs/ABS Nanocomposite

**EDAX and XRD**

EDAX analysis was performed to determine the elemental composition of the FNPs, the results of which are shown in Table 1 and Fig. 1. EDAX analysis of the FNPs (Fig.1A) and FNPs/ABS nanocomposite (Fig.1B) gave the weight percentages (wt%) of Fe and O with a ratio of ~1:0.72 in the FNPs and 1:2.3 in the FNPs/ABS nanocomposite.
Table 1: The chemical composition of the FNPs and FNPs/ABS.

<table>
<thead>
<tr>
<th>Element</th>
<th>FNPs Wt%</th>
<th>FNPs/ABS Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>41.75</td>
<td>10.96</td>
</tr>
<tr>
<td>Fe K</td>
<td>58.25</td>
<td>4.72</td>
</tr>
<tr>
<td>C K</td>
<td>-</td>
<td>84.05</td>
</tr>
<tr>
<td>Si K</td>
<td>-</td>
<td>0.1</td>
</tr>
<tr>
<td>Na K</td>
<td>-</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Figure 1. EDAX for FNPs (A) and FNPs/ABS (B).
The structure and average crystallite size of the FNP powder were determined by XRD. As shown in Fig. 2A, peaks were observed at 25.39°, 33.11°, 35.63°, 41.82°, 50.85° and 58.28°, corresponding to the (0 1 2), (1 0 4), (1 1 0), (1 1 3), (0 2 4) and (0 1 8) planes of Fe₂O₃, respectively. These results indicate the presence of a hexagonal hematite phase (JCPDS card No. 01-073-0603). The major XRD peak was located at 2θ ≅ 33.11°, whereas the second major peak was located at 2θ ≅ 35.63°. The other smaller peaks that were identified strongly suggest that hematite is the major phase in our sample. The XRD pattern also shows peaks at 20.91°, 35.63°, 44.89°, 52.32° and 74.67°, corresponding to the (111), (311), (400), (422) and (626) planes of magnetite (JCPDS card No. 01-086-1338), respectively, as a second phase.

The crystallite size can be calculated from the powder X-ray diffraction results by peak intensity analysis using the Scherrer formula, $D = \frac{K\lambda}{\beta\cos\theta}$, where $D$ is the crystallite size, $\lambda$ is the wavelength of X-ray radiation (Cu Kα1 radiation=1.54060 Å), $K$ is a constant, usually given as 0.9, $\beta$ is the full-width at half maximum (FWHM) after subtraction of the instrumental broadening and $\theta$ is the Bragg angle of the peak[14]. From the powder XRD pattern, the average crystallite size is found to be approximately 10 nm.

The structure of the synthesized FNPs/ABS nanocomposite was also characterized by XRD (Fig. 2B). The strongest peak at 21.48° correspond to pure ABS. The peaks at 26.5° (012), 35.84° (110) and 57° (018) correspond to the hematite phase while the peaks at 35.84° (311) and 52.8° (422) correspond to the magnetite phase, indicating that the FNPs were successfully incorporated into the ABS matrix.
SEM and TEM

Figure 3 shows SEM images of FNPs (A,B) and FNPs/ABS(C,D). The SEM images of the FNPs clearly show nanostructural homogeneities and spherical structured morphologies with an average size of 25–50 nm. Fig. 3(C,D) shows the SEM images of the FNPs/ABS nanocomposite thin film at 10 wt% FNPs concentration. The SEM images indicate that FNPs interspersed in the ABS matrix with a relatively uniform distribution and formed spherical FNPs. The FNPs are homogeneously dispersed in the polymer due to the modification of the surface of the FNPs prior to addition to the mixture of polymer and solvent (dichloromethane). After synthesizing FNPs by the co-precipitation method, the surface of the FNPs becomes hydrophobic and agglomerates. Thus, we modified the surface to become hydrophobic by using a mixture of carboxylic acid and dichloromethane to obtain a stable colloid. Then, the ABS solution was mixed with the previous colloid, which was cast in a petri dish at room temperature until the solvent was evaporated to safeguard the homogeneous dispersion in the polymer film. TEM images are shown in Fig. 4 to give further evidence on the morphologies and structures of the FNPs. The FNPs consist of small particles packed closely together, causing rough surfaces. The microstructures of the FNPs were studied by TEM. The morphology of the FNPs was found to be nearly spherical and the particle size of the FNPs was approximately 3.5 nm. This particle size is smaller than the particle size estimated by XRD and SEM due to the accumulation of nanoparticles indicated by dark sites in the TEM images.

![Figure 3. The SEM images for FNPs (A,B) and FNPs/ABS (C,D).](image1)

![Figure 4. The TEM images for FNPs.](image2)
Optical Properties

UV-Vis spectroscopy is a powerful technique for the identification of different optical transitions in a material. Energy band gaps can be determined by UV-Vis spectroscopy for applications such as optical fibres and optical coatings to inhibit corrosion, among others. The effect of added NPs on the absorption wavelength of the polymer is shown in Fig. 5a. The absorbance of pure ABS is greater than that of the FNPs/ABS nanocomposite and less than pure FNPs.

To determine the optical band gap of the FNPs, ABS and FNPs/ABS nanocomposite, we plotted $(\alpha h\nu)^2$ versus $h\nu$, where $h\nu$ is the photon energy and $\alpha$ is the absorption coefficient\(^\text{(17)}\), as shown in Fig. 5b. The band gaps of the FNPs, ABS and FNPs/ABS nanocomposite are 2.75 eV, 3.4 eV and 2.5 eV, respectively. The band gap of the FNPs agrees with the results from Route F. Majid et al.\(^\text{(18)}\). The results show that FNPs are blueshifted compared to bulk hematite (2.1 eV)\(^\text{(19)}\). Additionally, FNPs/ABS is redshifted compared to FNPs due to the addition of the nanoparticle filler in the polymer matrix\(^\text{(20)}\).

Thermal Analysis

Thermal stability is a significant property for polymeric materials. In general, thermal degradation of polymers can be improved by the addition of thermally stable nanofillers, such as Fe\(_2\)O\(_3\). The thermal properties of the FNPs/ABS nanocomposite films were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA analysis was used to study the thermal stability under both air and N\(_2\) atmosphere with a heating rate of 10°C min\(^{-1}\) and a flow rate of 50 ml/min by heating the FNPs/ABS nanocomposite from room temperature to 800°C. The degradation of pure ABS begins at 340°C and produces butadiene. Aromatics are observed at 350°C as a second degradation product. The evolution of acrylonitrile is the last degradation stage observed at 400°C\(^\text{(21)}\), under both air and N\(_2\). The degradation of FNPs/ABS nanocomposite under air and N\(_2\) was analyzed by TGA and DTG (derivative thermo-gravimetric), the curves from which are presented in Fig. 6. In air, it is obvious that FNPs/ABS degrades in two steps: the first step starts at 374°C and ends at 480.85°C and the second step occurs from 480°C to 800°C. For the degradation behaviour of the FNPs/ABS nanocomposites under N\(_2\), the curves have comparable shapes as those under air. The first step begins at 391.17°C and ends at 493.25°C and the second step occurs from 493.25°C to 800°C. The major weight loss incident occurs in the first step of the degradation. From the DTG curve, several overlapping peaks can be observed for the first degradation step, indicating that the first degradation is not a simple chemical reaction, but rather various reactions occurring together\(^\text{(21)}\).

S. Yang et al.\(^\text{(22)}\) applied TGA to investigate the degradation of pure ABS under air and concluded that pure ABS degrades in two steps. The first step starts at 180°C and ends at 620°C. For the degradation behaviour of pure ABS under N\(_2\), the TGA shows the first step occurring from 330°C to 450°C and the second step occurring from 450°C to 750°C. From the above results, we note that adding FNPs to the

![Figure 5. The optical absorption spectra for the FNPs, ABS and FNPs/ABS nanocomposite (a) and plot of $(\alpha h\nu)^2$ versus $h\nu$ for the FNPs, ABS and FNPs/ABS nanocomposite (b).](image-url)
to the ABS polymer increases its thermal stability. Improved thermal stability of FNPs/ABS nanocomposite films with respect to pure ABS can be assigned to the partially altered molecular mobility of the polymer chains due to their adsorption on the surface of FNPs. Additionally, FNPs have a considerable barrier effect to slow down product volatilization and thermal transport during decomposition of ABS, which helps composites with high thermal stability.[23] When comparing the residue of the FNPs/ABS nanocomposite film with that of the pure polymer results in ref.[22], we found that the addition of FNPs improved the residue of pure ABS from 0.6 to 2.92 wt% under air and from 0.3 to 2.24 wt% under N₂. The results showed that the residue under air (2.92 wt%) is greater than the residue under N₂ (2.24 wt%), which may be attributed to the presence of oxygen. The presence of oxygen seemed to change the decomposition mechanisms in the FNPs/ABS nanocomposite film. Generally, the initial stages of decomposition of FNPs/ABS under air and N₂ are similar. However, decomposition of FNPs/ABS under air involved an intermediate stage in which oxygen seemed to react with the
decomposing condensed phase to form a more thermally stable product. That product then decomposed slowly until the temperature increased sufficiently to substantially increase the rate of reaction between the condensed phase and oxygen\(^\text{[24]}\). As shown in Fig. 7, a 3.46 mg sample of the FNPs/ABS nanocomposite was analyzed via DSC from 40°C to 200°C under an inert atmosphere at a rate of 10°C min\(^{-1}\) with two heating stages. The glass transition temperature (Tg) of the FNP/ABS nanocomposite was measured from the second heating stage. There is a slight change in the Tg of the FNPs/ABS nanocomposite (108.29°C) compared to the Tg of pure ABS (102.00°C)\(^\text{[25]}\). The maximal shift of the Tg of approximately 6°C suggests a weak interaction between the FNPs and the ABS matrix. The above results show that the FNPs in the ABS matrix do not lead to the formation of chemical bonds between inorganic and organic phases\(^\text{[26]}\).

Figure 7. DSC analyses of the FNPs/ABS nanocomposite from the first and second heatings.
VSM

When particle size decreases below 30 nm, the magnetic properties of the particles change\[^{27}\]. The hysteresis loop of the FNPs and FNPs/ABS nanocomposite shown in Fig. 8 was measured at room temperature with a maximum applied magnetic field of 20 Oe using a vibrating sample magnetometer (VSM). The saturation magnetization (Ms) of the FNPs is 0.179 emu/g, the coercivity (Hci) is 24.8 G and the squareness is 12.38E-3, which is lower than the Ms (0.869 emu/g) and coercivity (191 G) for the FeOOH nanomaterials converted into hematite by the calcination method in ref.\[^{23}\]. However, for the FNPs/ABS nanocomposite, the saturation magnetization (Ms) is 33.83 emu/g and the coercivity (Hci) is 36.60 G at room temperature. When the coercivity approaches zero at room temperature, the nanoparticles have superparamagnetic behaviour\[^{28}\]. The superparamagnetic behaviour is dependent on the size of the particles, which is evidenced by a surface effect\[^{29-31}\]. The Ms value increases with increasing particle size. The Ms value of bulk hematite is 0.2 emu/g\[^{32}\], which is slightly higher than the Ms value for the FNPs prepared in this work. The saturation magnetization of pure FNPs is lower than that obtained for FNPs/ABS nanocomposite films (10% FNPs). Herein, the magnetic FNPs/ABS nanocomposite has been prepared by casting the mixture of FNPs and ABS, exhibiting saturation magnetization higher than that of FNPs.

This phenomenon can be explained by the “nano-network” structure and tight three-phase nanointerface\[^{33}\] (magnetite Fe$_3$O$_4$, hematite α-Fe$_2$O$_3$ and ABS). Nanocomposite films with such a “nano-network” structure and tight three-phase nanointerface show unexpected saturation magnetization, even higher than that of pure FNPs. There is no chemical reaction and no new compound through the casting process, so the unexpected saturation magnetization results from the physical structure in the FNPs/ABS nanocomposite films.

The results also indicate that the partition of the magnetic nanoparticles in the ABS causes the coercivity to increase due to the interactions between ABS chains and FNPs. Superparamagnetic materials have $M_r/M_s$ values < 0.01 and the squareness values of the FNPs and FNPs/ABS nanocomposite are 12.38E-3 and 18.24E-3, respectively. Additionally, the plot exhibits an S-shape, which confirms that our samples have superparamagnetic behaviour\[^{34}\]. The coercivity increased from 24.810 G for pure FNPs to 36.604 G after the nanoparticles were scattered in the polymer matrix. This result implies that the FNPs become harder (magnetically) after scattering into the polymer matrix. The enhanced coercivity of the FNPs/ABS nanocomposite results from the diminished interparticle dipolar interaction and the increased nanoparticle spacer distance for the single-domain nanoparticles, as contrasted with the nearby contact of the FNPs\[^{35}\].

![Figure 8. VSM analysis of FNPs and FNP/ABS nanocomposite.](image-url)
Conclusions

FNPs were synthesized by co-precipitation and nearly spherical nanoparticles were obtained. The average particle size of the FNPs was approximately 3.5 nm. The band gap value of the FNPs/ABS nanocomposite film was greater than the band gap of pure FNPs. The degradation of FNPs/ABS began at 391.17°C under N₂ and at 374°C under air when 10 wt% FNPs were added to the ABS as a nanofiller.

From the thermal study, we note that adding FNPs to the ABS polymer improves its thermal stability. A hysteresis loop of the FNPs and FNPs/ABS nanocomposite exhibited superparamagnetic behaviour and saturation magnetization of FNPs/ABS greater than that of FNPs due to the “nano-network” structure and tight three-phase nanointerface.

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References


