Fabrication of magnetic polymers from synthesized and commercial ferrofluids

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In this study commercially provided and laboratory synthesized ferrofluids which are a mixture of ultra-small magnetic particles in colloids were deposited on commercial hard disk media. The hard disk media which have different dipole moment densities were cut as 1.5 cm coupons and used as deposition under layers. To fabricate ferrofluid-polymer compositions deposited ferrofluids were transferred to polymers. Morphologies of the deposited coupons were studied by optical microscope and atomic force microscopy (AFM). Magnetic properties of the deposited polymers were investigated by a vibrational sample magnetometer (VSM). Structural characterizations of the synthesized ferrofluid nanoparticles were completed by an X-ray diffractometer (XRD).

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1. Introduction

Over the past several years, the preparation and characterization of the iron ferrite, Fe_3O_4, have attracted much attention as a traditional magnetic material used in magnetic storage media, solar energy transformation, electronics, ferrofluids, catalysis [1], magnetic contrast agent, and biomedical applications such as drug delivery, drug carrier and hyperthermia [2]. Fe_3O_4 powders can be synthesized by various methods such as hydrothermal synthesis, microemulsion, chemical co-precipitation, oxidation of $Fe(OH)_2$ by H_2O_2, R-ray irradiation and microwave irradiation [1].

Many studies about magnetic, electrical and ferromagnetic properties of the conducting polymer assemblies recently are of great interest, and studies about this kind of materials have become one of the most active and promising research areas [3].

Therefore, many researchers became interested in magnetic nanopowder-reinforced polymer composites because magnetic nanoparticles have a great potential for applications such as, aircraft, spacecraft, magnetic hard disks, and the magnetic part of credit cards. Also transferring of magnetic data pattern from hard disk media to polymer and formation of flexible magnetic polymers has been reported [4]. It is known that the behavior of magnetic particles in polymeric matrices has a great importance due to electronic, optical, and magnetic properties of these composites [5]. Magnetic particle-polymer composition applications can take advantage of both the magnetic properties and wear properties of these compositions [3]. For example, magneto-elastic behavior of magnetic field sensitive polymer gels can be used to fabricate soft sensors, switches and artificial muscles.

Today magnetic particle-polymer compositions are so attractive materials due to their potential to use in batteries, molecular electronics, electrical-magnetic shields and microwave-absorbing materials [3]. Until now, most commonly investigated magnetic nanoparticles were ferrofluids [6]. Ferrofluids can be defined as substituted ferrites in stable colloidal suspensions [6]. A literature survey revealed that there are many studies reported on synthesis of ferrofluids [6-12]. But, there are relatively few studies on fabrication of magnetic particle-polymer compositions [13-15]. It is known that the mechanism of dispersion of the magnetic nanoparticles in a polymer matrix is not fully understood and requires more research [6]. Therefore, it is essential to perform more effort and improve knowledge on the magnetic particle-polymer compositions.

Due to the importance of incorporation of magnetic particles and polymers with desired properties, this research focuses on synthesizing Fe_3O_4 ferrofluid nanoparticles and fabricating of ferrofluid-polymer (3-pyrrol-1-ylpropanoic acid or PPyAA) assembly.

In this study lab-made and commercially bought ferrofluids were individually used to fabricate magnetic polymers. These two groups of ferrofluids were compared for the capability of magnetic pattern transfer to polymers. Magnetic and morphologic properties of the magnetic polymers fabricated with different concentrations of ferrofluids were compared. The effect of ferrofluid concentrations on the magnetic and morphologic properties of the ferrofluid-polymer composition were investigated. By controlling the synthesizing process of

ferrofluids, composition of the ferrofluid-polymer assembly can be controlled.

The structural, magnetic and morphological studies of the samples were performed by X-ray diffractometer (XRD), optical microscopy, vibrational sample magnetometer (VSM) and atomic force microscopy (AFM) analyzes.

2. Materials and Method

2.1. Synthesis of ferrofluid Fe_3O_4 nanoparticles

Synthesis of the Fe_3O_4 nanoparticles carried out upon study of Sheparavoych *et al* [12]. All chemicals were of analytical grade. In a typical reaction 2.16 mM $FeCl_2.4H_2O$ and 4.32 mM $FeCl_3.6H_2O$ were mixed in deionized water and heated to 80°C under Argon atmosphere. 5 mM NH_4OH was added with injector during stirring of the substances. Solution was heated for 30 minutes and remained for cooling at room temperature. The magnetite precipitates were separated and washed several times with deionized water using magnetic decantation then 20 mL fresh deionized water was added. 1 mL NH_4OH was added to make the suspension alkaline. A mixture of 1 g citric acid and 2 mL deionized water was added to the solution at 60°C and stirred for 2 hours until nanoparticles were achieved. Distillation process was performed at 5 Krpm for 30 minutes with an ultra-centrifuge device. At the end of this process synthesized nanoparticles were become negatively charged and suspended in the carrier liquid.

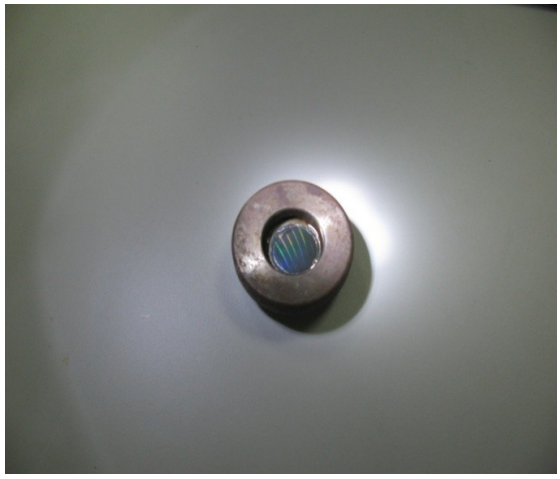
2.2. Deposition of ferrofluids on to hard disk coupons

Coupons with a diameter of 1.5 cm were cut from commercial pre-written hard disks (Seagate, Medalist 4310, Model ST34310A, 4,311 Mbytes). The reason for using pre-written hard disk coupons is to check transferring of the magnetic particles coated on the recorded data. The deposited magnetic particles in the ferrofluid attract by bits on the disk and allow orientation of magnetic particles by that data. For deposition of the ferrofluids, both synthesized and commercially provided (FerroTec-EMG 607) ferrofluids were used individually. Concentrations of commercial ferrofluids were adjusted to 1%, 3% and 5% by adding deionized water.

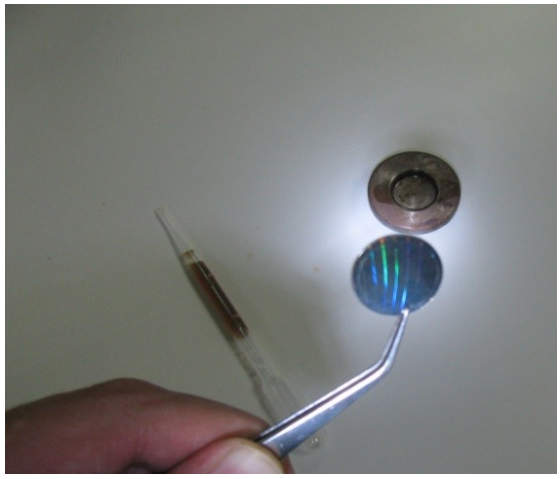
Prior to deposition, surface of hard disk coupons were cleaned with acetone and isopropanol respectively. For coating process ferrofluid was placed on to coupons, remained for 5 minutes and the remaining ferrofluid were pumped out. Later, coupons were placed in a Spin Coater (POLOS Spin 150) and spun with 2600 rpm for 5 minutes. Finally ferrofluid coated coupons were dried in air. A magnetic field was formed on the coupon surface caused by the bits located at the surface. After deposition, ferrofluids were oriented magnetically on the coupons by this magnetic field. It must be indicated that during deposition of ferrofluids no external magnetic field was applied. Only magnetic field of the hard disk media affected the ferrofluids. The orientation of deposited nanoparticles was observed with an optical microscope which detailed in the Results and Discussion section.

2.3. Fabrication of ferrofluid-polymer composition

After the optical microscope studies, deposited magnetic nanoparticles on the coupons were transferred to a thin polymer layer to fabricate the ferrofluid-polymer composition. During the transfer process no external magnetic field was applied similar as deposition of the ferrofluids.



(a)



(b)

Fig. 1. (a) Oriented magnetic particles on the coupons,(b) Ferrofluid-polymer composition

Firstly, ferrofluid coated coupons were put in the spin coater and commercially provided polymer (Disk Coat 4220, General Chemical Co. Brighton, MI) was placed on coupons. Subsequently coupons were spun at 2600 rpm for 30 seconds and dried in air for 20 minutes. Fabrication of the ferrofluid-polymer composition was completed by peeling the polymer layer with a circular adhesive tape. Fabricated magnetic polymer films were elastic and include a clear magnetic pattern of the disk data which

was observed from optical images and morphologic analyses. Magnetic nanoparticles on the polymer layer caused interference in thin films which can be observed by naked eye as seen in Fig. 1. Peeling of the magnetic pattern process from hard disk coupons to form magnetic polymer layer were repeated two more times for the same coupon. Magnetic analyses of the peeled polymer films indicated that, in the first peeling almost all magnetic particles were transferred to the polymer layer. Second and third peeled polymer films showed very low, almost zero magnetism according to VSM analyses.

2.4. Characterization of the samples

Polymer–magnetic nanoparticle assembly, both fabricated with commercial and laboratory synthesized ferrofluids were characterized by various methods. Crystal structure of the synthesized ferrofluids was analyzed with a Rigaku X-ray diffractometer (XRD). Magnetic pattern that transferred from hard disk coupon to the ferrofluid-polymer composition was imaged with a Nikon ECLIPSE MA100 model optical microscope. Surface morphology of the coated ferrofluids with various concentrations was examined with Park Systems XE-100E model atomic force microscopy (AFM). Magnetic properties of ferrofluid-polymer composition was analyzed by a Quantum Design Physical Property Measurement System (PPMS 9T) vibrational sample magnetometer (VSM). Analyze results were confirmed successful synthesis of the ferrofluids and combination with the polymer according to similarity of results obtained from commercial ferrofluids.

3. Results and discussion

3.1. Crystal structure analyze

Liquid in the synthesized ferrofluids was vaporized and remaining magnetic powder was analyzed with a XRD (Rigaku). X-ray analyze result of the synthesized nanoparticles is displayed in Fig. 2. Standard diffraction spectrum (JCPDS: 65–3107) was confirmed formation of the Fe_3O_4 crystals in the synthesized ferrofluid [1]. Results were indicated synthesized Fe_3O_4 crystals have a preferred orientation of (311). Sharpness and intensity of the main diffraction peak represents highly crystalline structure of the sample.

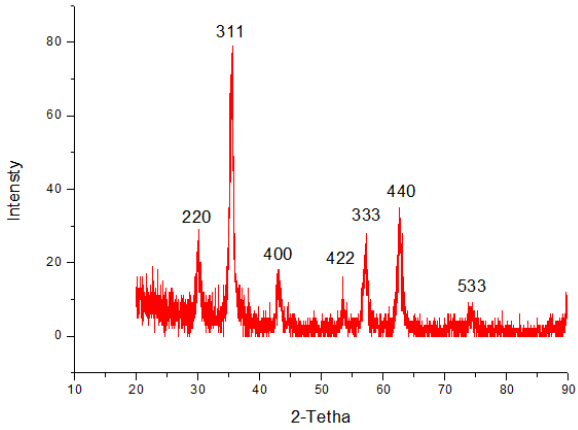


Fig. 2. X-ray pattern of the synthesized ferrofluid

3.2. Optical analyzes of oriented ferrofluids on the coupons

To observe orientation of the magnetic nanoparticles on the hard disk bits, samples were imaged with an optical microscope prior to polymer deposition. It is known that commercial hard disk media contains servo sectors that separate data regions to keep recording heads truly placed on data tracks [3]. Servo sectors of the disk are magnetic marks to make reading-writing processes properly. Observing these sectors of the disk in the deposited particles allow confirmation for orientation of the magnetic particles by magnetic pattern of the disk. As displayed in the images, spread and orientation of the ferrofluids on the data and servo sectors of the disk media were very successful. Magnetic nanoparticles were embedded on coupons very regularly as seen in Fig. 3.

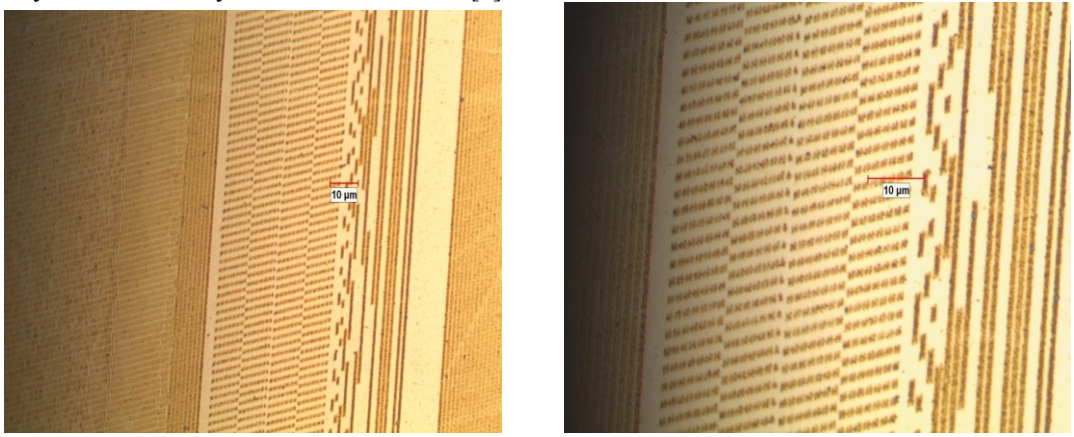


Fig. 3. Optical images of ferrofluids on the coupons with various magnifications

3.3. Optical analyzes of ferrofluid-polymer compositions

After imaging of hard disk coupons, ferrofluid-polymer composition was analyzed with the optical microscope to observe magnetic layer transferred to the polymer films. Optical microscopy images of the ferrofluid-polymer compositions are given in Fig. 4. According to the analyze results transfer of magnetic pattern from hard disks to polymer films were successful. Data and servo sectors was clearly observed on the polymer layer.

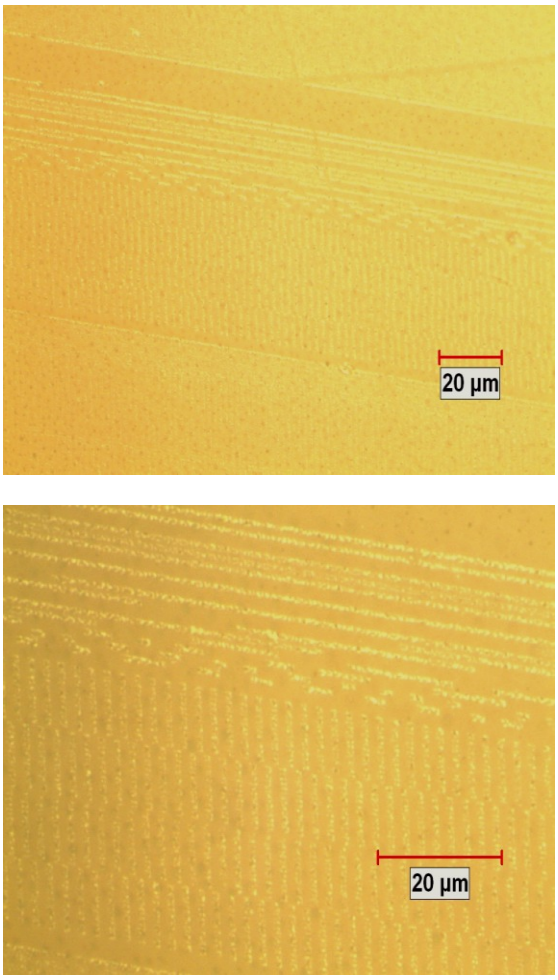


Fig. 4. Optical images of ferrofluid-polymer composition with various magnifications

3.4. Magnetic analyzes

Magnetic properties of the ferrofluid-polymer compositions were analyzed by a vibrational sample magnetometer (VSM). Magnetism of samples fabricated with various concentrations of synthesized and commercially provided ferrofluids solutions were investigated with VSM.

According to analyze results, all fabricated samples showed magnetic hysteresis with various magnitude of magnetizations. Also uncoated single polymer was analyzed with VSM, and no magnetization was observed as expected.

In Fig. 5a VSM analyze results of ferrofluid-polymer compositions coated by ferrofluid concentrations of 1% (curve a), 3% (curve b), 5% (curve c) and uncoated polymer (curve d) were presented. As seen in the curve b, highest magnetization was observed from polymer coated with 3% ferrofluid solution. Curve c represents ferrofluid with 5% concentration which shows a low magnetism then ferrofluid with 3% and %1 concentration. As observed with curve a, ferrofluid with 1% concentration shows very low magnetism which can be considered almost zero. Curve d represents the uncoated polymer, which shows zero magnetism. Zero magnetism of single polymer confirms transfer of the magnetic pattern. It is suggested that 1% ferrofluid solution contains very few magnetic particles to deposit on coupons and polymer layer also. Therefore deficiency of the magnetic particle results deficiency of adherence and a poor formation of the magnetic layer on the coupons. It is a little surprising result that 5% ferrofluid shows less magnetization then 3% ferrofluid. This behavior can be explained by excess of magnetic particles after a critical value may result stack of magnetic particles which ruins formation of the magnetic pattern. It is suggested that in our study 3% ferrofluid concentration have appropriate amount of magnetic particle and a critical value for concentration, which confirmed with atomic force microscopy analysis given in the next section. Probably, this critical ferrofluid concentration allows to uniform spread of magnetic particles on the surface of the disk which results transform of the deposited magnetic particles with high efficiency.

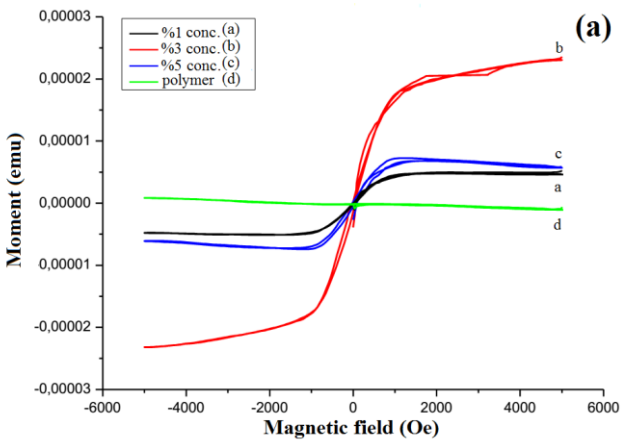


Fig. 5a. Magnetic hysteresis of polymer coated with ferrofluids of various concentrations

Due to best magnetization of magnetic polymer was achieved from 3% ferrofluid solution, for further magnetization analyzes, polymer-ferrofluid samples coated with 3% ferrofluid solutions were used.

In Fig. 5b and 5c VSM analyze results of the polymers coated with 3% ferrofluid solutions were shown. Fig. 5b displays VSM analyses of polymer-ferrofluid composition coated with commercially provided ferrofluid. It was observed that magnetization of the sample reached highest value at magnetic field of nearly 1 kOe. Maximum saturation magnetization value was measured as approx. 2.10^{-5} emu. In the figure curve a represents first peeled polymer layer from the coupon for magnetic analyze. Red (curve b) and blue (curve c) curves second and third peeled polymers respectively. As seen from the figure almost all magnetic layer deposited on coupon was peeled in the first time. According to magnitude of magnetic moment in the hysteresis analysis, nearly 96% of magnetic particles were transferred to polymer film in the first peeling.

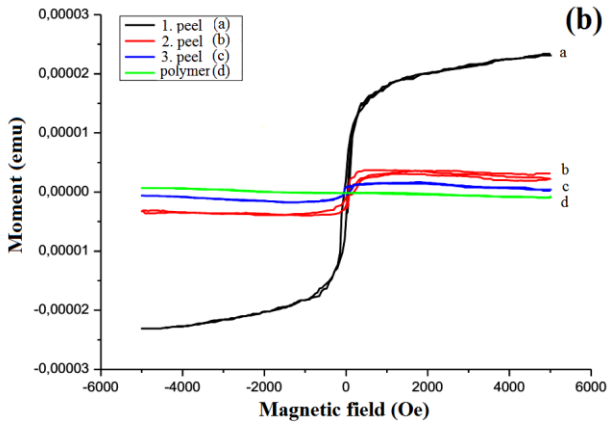


Fig. 5b. Magnetic hysteresis of the hard disk coupon coated with the commercially provided ferrofluid

In Fig. 5c VSM analyze of polymer-ferrofluid composition prepared by lab-synthesized ferrofluid is given. According to the Fig. 5c it can be said that almost all deposited magnetic particles were transferred to the polymer with the first peel as in the commercial ferrofluid (Fig. 5b). The curve belongs to the first peeled layer (curve a) demonstrated a magnetic behavior. Magnetization of this sample was reached the highest value at magnetic field of about 1 kOe, which was same as commercially provided ferrofluid. Also maximum saturation magnetization value was approx. 2.10^{-5} emu, which was again similar with magnetic polymer fabricated with commercially provided ferrofluid. Furthermore, curves belong to second and third peeled polymers (curve b and c) showed a very low magnetism. Probably remaining magnetic particles on the coupon after the first peel carried a small magnetism to the polymer layers in the second and third peel.

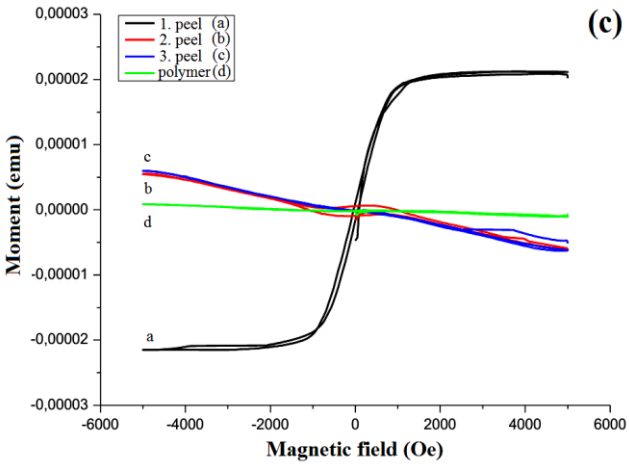


Fig. 5c. Magnetic hysteresis of the hard disk coupon coated with the lab-synthesized ferrofluid

According to VSM analysis results it can be clearly stated that lab-synthesized ferrofluid exhibit almost same magnetic behavior with commercially provided ferrofluid.

3.5. Morphologic analyses

Morphologic analyses of the coupons coated with various ferrofluid concentrations were examined by AFM. In the Fig. 6 AFM images of ferrofluid-polymer composition coated with lab-synthesized and commercially provided ferrofluid concentrations of 1%, 3% and 5% were presented.

As seen in the AFM images, fabricated samples were indicated successfully orientation of magnetic data on the hard disk coupons for both laboratory synthesized and commercially provided ferrofluids.

In the Table 1. surface morphology parameters of samples are listed in detail. R_q value represents the difference between the highest and the lowest points of the surface. R_p is the value of the highest point. R_z indicates average roughness of 10 random points on the surface. Low values of the morphologic parameters R_q, R_p, R_{sk}, R_z and R_{ku}, mostly indicate roughness of coatings. According to determined parameters, a denser coating was achieved with ferrofluid solution of 3% concentration. This result is in accordance with magnetization results of magnetic polymer fabricated with 3% concentration. Also surface of polymer coated with 1% ferrofluid concentration was more smooth and rough.

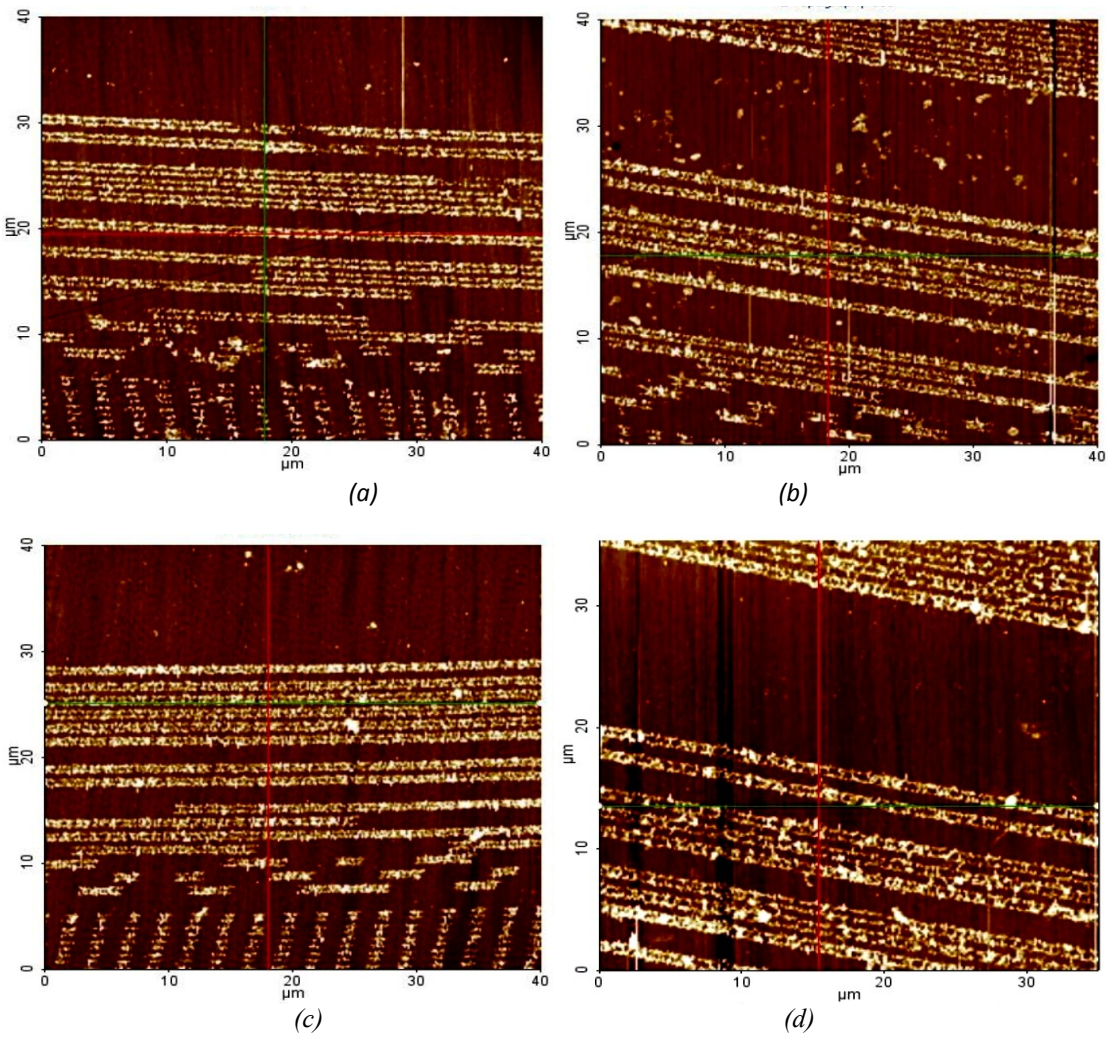


Fig. 6. AFM images of hard disk coupons coated by (a) commercially provided ferrofluid, 1% conc. (b) commercially provided ferrofluid, 3% conc. (c) commercially provided ferrofluid, 5% conc. (d) lab-synthesized ferrofluid.

Table 1. Morphologic parameter values of ferrofluid coatings

SOLUTIONS	R_a (nm)	R_q (nm)	R_p (nm)	R_{sk} (nm)	R_z (nm)	R_{ku} (nm)
Commercial ferrofluid 1%	6.546	12.154	120.176	-5.037	54.999	36.545
Commercial ferrofluid 3%	11.460	16.389	153.404	-2.176	96.160	11.118
Commercial ferrofluid 5%	11.292	14.232	76.742	-1.131	66.433	4.315
Synthesized ferrofluid 3.9%	11.137	17.625	142.513	-3.360	74.567	18.484

4. Conclusions

In this study, synthesizing of ferrofluids for fabricating magnetic polymers was described. XRD analysis of the synthesized ferrofluid confirmed formation of Fe_3O_4 nano crystals. Synthesized ferrofluids and commercially provided ferrofluids were successfully deposited on the hard disk coupons to compare magnetic transfer ability of the synthesized ferrofluids. Both commercially provided and lab-synthesized ferrofluids were attracted by bits on the surface and oriented magnetically on the hard disk coupons. Orientation of both ferrofluids on the coupons indicates a successful transferring of magnetic pattern from hard disk media to the polymers. Also magnetic pattern transferring was confirmed by optical and atomic force microscopy analysis. The effect of different ferrofluid concentrations on the magnetic and morphologic properties of polymer-ferrofluid composition was examined. Magnetic polymer films were fabricated by various ferrofluids concentrations. Magnetic polymer fabricated with 3% ferrofluid concentration exhibited a denser and fine

ordered magnetic layer. VSM analysis of coated ferrofluids (both commercially provided and lab-synthesized) confirmed that the synthesizing and transferring process of ferrofluids to polymer layer were successful. The results of experiments have a potential to encourage more studies on fabrication of thin, flexible magnetic polymers by controlling the magnetic fluid composition.

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