

Preparation and Characterization of Some Magnetic Nanocomposites of Biodegradable Polyurethane Based on (s)-histidine

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Recycling the polymeric materials into the cycle of nature is one of the concerns of scientists; this has been possible through using natural or synthetic polymers. In this study, new polyurethanes containing optically active monomers and ester linkages were developed by prepolymer method. Nano zero valent iron (ZVI) particles that were synthesized by co-precipitation method, were well dispersed in the polymeric matrix with different percentage amounts in the presence of the ionic liquid via in-situ polymerization technique. The accuracy of monomer synthesis, all prepolymers and polyurethanes was confirmed by typical spectroscopy techniques of FTIR, ¹HNMR, and CHN-O elemental analysis. To study the quality of ZVI and nanocomposites, nanoparticles (NPs) distribution instrument of X-ray (XRD), and scanning electron microscopy (SEM) were used. Properties such as thermal stability and thermal behavior and magnetic field were examined respectively by TGA, DTG, DSC and VSM techniques. Hydrolytic and enzymatic degradation of polyurethane composites with different weight percentages of Fe₃O₄ were studied.

Key words: Biodegradable; Polyurethane; Magnetic, Nanocomposite.

Polyurethanes are versatile polymers made of very soft foams to hard elastomers and, durable coatings in applications as diverse as medical, pharmaceutical, paint and coating industries¹. From the reaction of Diisocyanate with diacids and polyols, they are easily prepared in a polyaddition reaction. Polyester-polyols or polyether-polyols with different aliphatic and aromatic structures are synthesized for this purpose². Generally, the structure-property relationships in a Polymer chain with its final characteristics is confirmed³. Depending on the type of requirements and the usages of special

soft⁴ or hard⁵ segments, optically active side branches⁶, ether bonds⁷, ester⁸⁻⁹, amide and imide¹⁰ functional groups are used to solve some polyurethane difficulties such as low thermal stability and poor mechanical strength¹¹. With the increasing free spin rotation of polymer chains, ether links make them more flexible. By creating hydrogen bonds through amide groups, increase the solubility of the product¹². Also the repetition of amide groups and the heterocyclic rings in polymer chains, improve the heat resistance of the polymers¹³. The presence of ester bonds in the polyurethane's structure increases the likelihood of hydrolytic degradation in esterase¹⁴. Not returning to the cycle of nature is one of the issues that synthetic polymers are faced with. Natural polysaccharide-based biodegradable polymers

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such as chitosan and alginate¹⁵, although are used in the food and pharmaceutical industries, do not have the durability and thermal stability. Due to their potential applications in fields related to human life such as health and environmental protection, biodegradable polymers, in the last twenty years, have been regarded by researchers. Using biocompatible amino acid groups in the polymer chain structure, increases the solubility and causes the development of the applications as drug delivery agents¹⁶, detection of chiral and isolation of enantiomers in stationary phase of chromatography¹⁷, asymmetric synthesis catalyst, absorbent metal ions and biomaterials¹⁸. In an efficient way, the structure of optically active amino acids is entered into chemical structures of diol or diacid and used as a monomer to prepare polymers¹⁹⁻²³. It is expected that such synthetic polymers based on amino acids, are biocompatible and biodegradable. Invasion of microorganisms and fungi in soil and water of the sea or in the presence of esterase enzymes in in-vitro conditions has shown that the polyester-polyurethane compared with polyether-polyurethanes have greater biodegradability²⁴⁻²⁹. In addition to the structural modification of polyurethane chain, we can use inorganic nanoparticles, such as metal oxides, for example TiO₂³⁰, ZnO³¹, SiO₂³² and Fe₃O₄³³⁻³⁵ to improve the required features. For example, the nanoparticle of zero-valent iron oxide (ZVI), although is now investigated in many articles, the application of it is regarded. Recently magnetic composite of polyurethane / Fe₃O₄ are produced and in some of them nanoparticles of Fe₃O₄ are used without surface modification and emulsifier capacity. Such as the research of xu and et.al³⁶ as well as Guo and et.al who developed polyurethane magnetic composites as microwave absorbers³⁷. Surface modification of Fe₃O₄ nanoparticles with thiacalix⁴ arenes (TC4As)³⁸ or TDGA have been reported by Mohammadi and et.al. They state that nanocomposites based on polyurethane with a more appropriate distribution of magnetic nanoparticles are biocompatible and non-toxic, so they are a good candidate for being used in biomedical applications³⁹. In a study, covered Fe₃O₄ nanoparticles with bamboo carbon were used to destruct the quinoline in the treatment of a wastewater through "immobilized cell" method⁴⁰. In another article magnetic nanoparticles coated

with polyurethane are employed as a carrier immobilized microorganism for removing toluene and phenol from wastewater in a treatment. The magnetic field causes the degradation of phenol by accelerating the growth of microorganisms. Weak magnetic fields can stimulate bacterial growth effectively, shorten the cycle of growth and increase the activity of microorganisms that are useful for reproduction and metabolism⁴¹. In this paper, some new biodegradable polyurethane nanocomposites were prepared. With an optically active monomer based on (s)- histidine, some optically active polyester-polyurethane containing amide groups were prepared and then Fe₃O₄ magnetic nanoparticles in different weight ratio dispersed in the polyurethane chains using ionic liquid. The accuracy of synthesis, thermal and magnetic properties, and biodegradability of nanocomposites were investigated.

EXPERIMENTAL

Materials

N-methyl-2-pyrrolidone (NMP; 99.5%), triphenyl phosphite (TPP; 98%), (s)-histidine monohydrochloride monohydrate (98%), and absolute ethanol (99%), methanol (98%), pyridine (py, 99%), 4,4'-Methylene-bis-(4-phenylisocyanate) MDI, Hexamethylene diisocyanate (HDI, 99%), calcium chloride, dibutyltin dilurate (DBTD, 97%), ethylene glycol (EG), hydroquinone (HQ), terephthaloyl dichloride (TPC, 98%), dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), FeSO₄·7H₂O, and FeCl₃·6H₂O salts were obtained from Merck Co. Tosyl chloride (Aldrich, 99%), adipoyl chloride (Aldrich, 98%), and 1,2,4-benzenetricarboxylic acid 1,2-anhydride (TMA; 98%) was purified by recrystallization from the mixture of acetic anhydride and acetic acid (1:5). N,N-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over barium oxide prior to polymerization. The other materials were used as obtained without further purification.

Techniques

Infrared measurements were performed on a Bruker-IFS48 FTIR spectrometer (Ettlingen, Germany). The spectra of solids were carried out using KBr pellet. Vibrational transition frequencies are reported in wave numbers (cm⁻¹). Band

intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Proton nuclear magnetic resonance ^1H NMR (500 MHz) spectra were recorded in DMSO- d_6 solution using a Bruker Avance 500 (GmbH, Germany). Tetramethyl silane (TMS) was used as an internal reference. Multiplicities of proton resonance are designated as singlet (s), doublet (d), doublet of doublet (dd) and multiplet (m). Elemental analyses were performed by a CHN-O Rapid Heraeus elemental analyzer (Wellesley, MA). Inherent viscosities were measured by a standard procedure using a Cannon Fenske Routine Viscometer (Germany) at a concentration of 0.5 g dL $^{-1}$ in NMP at 30°C. Differential scanning calorimetric (DSC) and thermogravimetric analysis (TGA) were recorded in nitrogen atmosphere at a heating rate of 30°C/min on a Stanton Redcraft STA-780 (London, UK). Specific rotations were measured by a Perkin Elmer-241 Polarimeter (Germany). Wide angle X-ray diffraction patterns (XRD) were performed at room temperature on an X-ray diffractometer (Siemens model D 5000, Germany) using Ni-filtered CuK α radiation (40 kV, 25 mA) with scanning rate of 3°/min. The morphology of the polyurethane (PU)/Fe $_3$ O $_4$ nanocomposites powders during milling was investigated by means of scanning electron microscopy (SEM; Philips, XL30) on gold-coated powders. The magnetic properties of Fe $_3$ O $_4$ nanoparticles and composites were studied with Vibrating sample magnetometer (VSM) by Central Laboratory of kashan university (Isfahan-Iran).

Methods

Preparation of magnetic Fe $_3$ O $_4$ nanoparticles

The typical synthesis procedure of Fe $_3$ O $_4$ nanoparticles is similar to the method described in⁴¹. Twenty grams NaOH was dissolved in 250 mL deionized water which was deoxygenated by bubbling N $_2$ gas for 30 min at 1,000g stirring for 10 min. In another beaker, 0.85 mL of 12.1 N HCl and 25 mL deionized water was mixed, and then 8.1 g of FeCl $_3$.6H $_2$ O and 3.1 g of FeSO $_4$.7H $_2$ O were successively dissolved in the solution under stirring. Then, the resultant solution was added drop-wise into the above-mentioned NaOH solution under vigorous stirring, and black precipitate was obtained and harvested by centrifugation, and then washed with deionized water and ethanol several times, respectively, and finally dried in the air at 80°C for 2 h. Then, the

harvested Fe $_3$ O $_4$ nanoparticle composite was used for the next step in the preparation of the magnetic PU/Fe $_3$ O $_4$ composites.

Synthesis of diacids

In this step first, 0.351 g of (s)-histidine (2 mmol) were stirred in 8 ml of NMP at 0 °C for 30 minutes. A 50 mL, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, and calcium chloride drying tube was charged with the mixture. Then about 1.0 mL of propylene oxide was added, and after a few minutes 0.183 g of adipoyl chloride (1 mmol) was added. The temperature was raised to room temperature and the solution was continuously stirred for 6 hrs. Polyamide was precipitated by pouring the flask content into methanol. Then it was filtered, washed with hot water and methanol and dried overnight under vacuum at 100 °C. (Terephthaloyl chloride was used in the same way.) Two types of diacid as chain extender were prepared in this step. The yield of APC diacid 84.5% and TPC diacid 95.0%, and their specific optical rotations, $[\alpha]_{25\text{D}}$: -78.6 and -55.9 [0.0520 g and 0.0500 g in 10 mL of DMF] were obtained.

Synthesis of polyester-polyols

To prepare the polyester - polyol oligomers or diol containing ester linkages, first, the catalytic solution contains 1.068 g (5.6 mmol) of tosyl chloride in 2 ml of pyridine was stirred for half an hour and then 2 ml of DMF as solvent was added to the mixture. In a case that EG was used in diol synthesis, 0.744 g (1.2 mmol) of ethylene glycol and to provide diol solution with HQ, 0.132 g (1.2 mmol) of hydroquinone, were dissolved in 1 ml of pyridine. To prepare the solution of dicarboxylic acid, 0.548 g (1 mmol) of the synthesized diacid in the previous step was dissolved in 4.5 ml of DMF. Finally, the acid solution was poured in a 50 ml, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, and condenser, and then catalyst solution was gradually added within 20 minutes to the flask solution. The diol solution was then added to the mixture and stirred for half an hour. Then, the temperature was increased to 120°C and stirred at this temperature for 2 hours continuously. The resulting product was work up with pouring in to 50 ml of water and methanol (1:1) and stirring for 15 minutes. Finally, the resulting precipitates filtered, washed with water and then dried for 2 hours at 80°C in a vacuum

oven. Four different kinds of polyester-polyols were synthesized in the same way.

Synthesis of polyurethanes

At each batch, a solution of 0.1 mmol of polyester-polyol derived from the previous step with 0.025 g (0.1 mmol) of MDI or 0.017 g (0.1 mmol) of HDI in 1 ml of NMP as solvent was prepared and 0.01 grams of catalyst (DBTD) was added to the mixture then, mixed for 30 minutes at room temperature. The temperature gradually increased to 110 °C and the reaction was completed in 7 hours. The resulting mixture was cooled and was poured in 100 ml of water. So polymer precipitates were isolated in water and separated. Finally, they dried at 90 °C in the vacuum oven. Generally, 8 samples of polyurethanes were prepared this way.

Preparation of polyurethane/Fe₃O₄ nanocomposites

According to the yield at each batch, the required amounts of raw materials, solvents and catalyst for preparing one grams of polyurethane were calculated. Before curing stage, using catalyst, the amount 0.1 g of synthesized Fe₃O₄ nanoparticles and 0.1 g of ethyl methyl imidazolium bromide ionic liquid; [emim]Br were added to the solution and distributed by sonication method. Therefore, NPs in the in-situ polymerization were

entrapped between the polymer chains during the polymerization to form a desirable composite. All nanocomposites were fine synthesized in the same way with different weight percentages up to 30% of NPs in the polymeric matrix.

RESULTS AND DISCUSSION

Optically active co-poly(ester amide urethane)s were prepared in three stages from chemical reactions. Two new optically active acids were synthesized from the reaction of (s)-histidine with adipoyl chloride or, terephthaloyl chloride in 1:1 molar ratio. Calcium chloride as water absorbent and propylene oxide as acid scavenger are used. Amide bonds were formed at this reaction step. Imidazolium side branch as polar heterocyclic rings and amide bonds are the advantages of this design of diacid, addition to the optically active properties.

Characterization of diacids

In Figure 1 the FT-IR spectra of optically active diacid based on APC are shown. Peaks in the range of 3410-2925 cm⁻¹ are related to the C-H bond stretching frequency, peaks in the range of 2345 cm⁻¹ to amide N-H stretching frequencies, spectrum in 1620 cm⁻¹ to the frequency of the aromatic C=C bond stretching and distinct peak in

Table 1. Characterization of diacids

Diacid Type	Formula [Mw]	FT-IR (cm ⁻¹)	¹ H-NMR	Elemental analysis	
				Calcd.	Found
APC	C ₁₈ H ₂₄ N ₆ O ₆ [420]	3410-3607 (O-H) acid, 2925- 3410 (C-H), 2345 (-NH-) amide & imidazolium, 1683 (C=O) acid, 1620 (C=C) arom. & (C=O) amide, 1150 -1095 (C-H) aliph. 1008 (C-C) aliph.8	1.35 dd (4H, CH ₂); h 1.87 d (4H, CH ₂); g 3.50 dd (4H, CH ₂); f 5.12 d (2H, CH); e 7.52 d (2H, aromatic);d 8.28 s (2H, N-H aromatic); c 8.54 dd (2H, arom.);b 14.31 s (2H, acid); a 8	C: 51.43 H: 5.71 N: 20.00	C: 51.38 H: 5.70 N: 19.89
TPC	C ₂₀ H ₂₀ N ₆ O ₆ [440]	3560 (O-H) acid, 3000- 3410 (C-H), 2235 (-NH-) amide & imidazolium, 1600 (C=O) acid, 1575 (C=C) aromatic & (C=O) amide, 1165 (C-H) aliphatic 1005 (C-C) aliphatic 8	3.52 dd (4H, CH ₂); g 5.25 d (2H, CH); f 7.60 d (2H, aromatic);e 7.87 s (4H, benzene);d 8.35 s (2H, N-H aromatic); c 8.67 dd (2H, arom.);b 14.31 s (2H, acid); a	H: 4.54 N: 19.09	H: 4.52 N: 19.01

1683 cm⁻¹ can be attributed to stretching and amide and acid carbonyl groups. Peaks in the range of 1150-1008 cm⁻¹ can be assigned to the aliphatic C-C bonds and C-H stretching frequencies.

The nuclear magnetic resonance spectrum (¹H-NMR) of optically active diacid (APC) can be seen in Figure 2. As it shown, amine hydrogen (N-H) and C-H bond between two second types of amines in (s)-histidine around 8.3 and 8.4 ppm, it's aromatic hydrogen in 7.4 ppm, optically active C-H bond in 5 ppm, methylene (CH₂) histidine in range of 3.4 and 3.5 are located. Peaks related to hydrogen nuclear magnetic resonance of aliphatic methylene groups have appeared on the lower fields, in the range of 1 and 1.7 ppm.

Characterization of prepolymers

The reaction of an optically active diacid obtained from the previous step with one of two commercial diols, EG and HQ when the molar ratio of alcohol is higher than the diacid, causes to prepare some new diols, polyols and hydroxyl end groups oligomers. Ester bonds were formed at this step (fig.3).

CHN-O elemental analysis of two kinds of diacid, four types of diols and eight samples of polyurethanes which confirm validity of their synthesis were shown in Tables 1 and 2. Polyurethanes containing amide and ester groups, and imidazolium side branches were synthesized by the reaction of the prepared prepolymers with commercial diisocyanates, HDI and MDI in the presence of a DBTD as catalyst and the gradual elimination remove of water.

Characterization of polyurethanes (PUs)

FTIR, ¹H-NMR spectra, and elemental analysis of PUs

The resulting PUs were characterized by FTIR, ¹H-NMR and elemental analysis techniques. The data were shown in Table (2) and figure (5). All the polymers showed two almost broad characteristic FTIR absorption peaks at about 3050-3420 cm⁻¹ related to amide N-H bands, and 1648-1661 cm⁻¹ corresponding to the amide carbonyl and ester groups. It showed be mention that the broadness of peaks was attributed to the preformed

Table 2. Characterization of diols and polyurethanes

Comp.	Code	Formula	Mw	Type	Elemental analysis		
					C (%)	H (%)	N (%)
Diol	APC-EG	C ₂₂ H ₃₂ N ₆ O ₈	508	Calcd.	51.97	6.30	16.53
				Found	51.90	6.21	16.50
	APC-HQ	C ₃₀ H ₃₂ N ₆ O ₈	604	Calcd.	59.60	5.30	13.91
				Found	59.71	5.35	14.01
	TPC-EG	C ₂₄ H ₂₈ N ₆ O ₈	528	Calcd.	54.54	5.30	15.91
				Found	54.49	5.25	16.00
	TPC-HQ	C ₃₂ H ₂₈ N ₆ O ₈	624	Calcd.	61.54	4.49	13.46
				Found	61.60	4.46	13.30
Polymer	APC-EG-HDI	C ₃₀ H ₄₂ N ₈ O ₁₀	674	Calcd.	53.41	6.23	16.62
				Found	54.01	6.15	17.33
	APC-EG-MDI	C ₃₇ H ₄₀ N ₈ O ₁₀	756	Calcd.	58.73	5.29	14.81
				Found	60.00	5.30	15.02
	APC-HQ-HDI	C ₃₈ H ₄₂ N ₈ O ₁₀	770	Calcd.	59.22	5.45	14.54
				Found	60.08	5.42	14.53
	APC-HQ-MDI	C ₄₅ H ₄₀ N ₈ O ₁₀	852	Calcd.	63.38	4.69	13.14
				Found	63.45	4.65	13.11
	TPC-EG-HD	C ₃₂ H ₃₈ N ₈ O ₁₀	694	Calcd.	55.33	5.48	16.14
				Found	55.28	5.43	16.02
	TPC-EG-MDI	C ₃₉ H ₃₆ N ₈ O ₁₀	776	Calcd.	60.31	4.64	14.43
				Found	60.51	4.66	14.62
TPC-HQ-HDI	C ₄₀ H ₃₈ N ₈ O ₁₀	790	Calcd.	60.76	4.81	14.18	
			Found	60.78	4.84	14.08	
TPC-HQ-MDI	C ₄₇ H ₃₆ N ₈ O ₁₀	872	Calcd.	64.68	4.13	12.82	
			Found	64.50	4.30	12.49	

amide units and also polyamide backbones. The representative FTIR spectra of TPC-EG-HDI PU were brought in Figure 5. Not so broad peak in the area 3403 cm^{-1} , secondary amines N-H stretching frequency in the structure of histidine, peaks in the frequency range of $3403\text{-}2923\text{ cm}^{-1}$ tensile C-H bond, peaks in the range of 2300 cm^{-1} stretching frequencies N-H amide, peak in an area 1600 cm^{-1} is related to stretching frequency of the aromatic C=C bond stretching, amide carbonyl groups, created peak in area 1775 cm^{-1} is attributed to the ester carbonyl, and peaks in the range of $1244\text{-}1009\text{ cm}^{-1}$ return to stretching frequency of the aliphatic C-C and C-H bonds in ethylene and adipoyl. The absence of sharp peaks in the area 2270 cm^{-1} , the stretching frequency of NCO indicates the purity of polyurethane without diisocyanate as raw material. Presence of a peak in the area 1718 cm^{-1} , related to tensile frequency of polyurethane carbonyl groups proves the synthesis accuracy of the polymer.

The $^1\text{H-NMR}$ of TPC-EG-HDI PU showed peaks in the region of $\delta = 7.55\text{-}8.79$ ppm related to aromatic rings, and peaks for two kinds of amide and urethane NH groups appeared as singlet at $\delta = 10.57$ and 10.28 ppm. The other polymers showed similar peaks in the $^1\text{H-NMR}$ spectra with differences in aromatic and aliphatic proton magnetic resonance fields. The elemental analysis results were in good agreement with calculated

percentages for carbon, hydrogen and nitrogen contents in poly(ester-amide-urethane)s (PEAUs) repeating unit (Table 2).

Solubility of PUs

The solubility properties of PEAs were studied in different solvents (Table 3). Polymers were soluble in the polar aprotic solvents such as NMP, DMAc, DMF, DMSO, and m-cresol. The solubility of the polyesters was in the range of 2.1-2.8 g/dL. Good solubility of the polymer was mainly related to the presence of ester units, optically active groups, and polar (s)-histidine bulky pendant from diacid moieties. Difference in solubility of PUs was based on the structure of diol and diisocyanate moieties in the polymer backbone. The APC-EG-HDI PU and APC-EG-MDI PU showed better solubility due to the fact that the related diols contained aliphatic bonds and were more flexible.

Yield, inherent viscosity, and specific rotation of PUs

Yields and inherent viscosities of obtained polymers via three different methods were compared and the results were differences in values. As the inherent viscosity is a good criterion for estimation of molecular weight, it was concluded that all the polymers showed reasonable molecular weights. Another important outcome was PUs obtained with aromatic linkages had higher viscosity and molecular weight in comparison to fully aliphatic ones.

Table 3. Solubility of poly(ester-amide-urethane)s

Diacid Diol Diisocyanate	Compound							
	APC				TPC			
	EG		HQ		EG		HQ	
	HDI	MDI	HDI	MDI	HDI	MDI	HDI	MDI
Solvent	Solubility of polyurethanes							
DMAc	+	+	+	+	+	+	+	+
DMF	+	+	+	+	+	+	+	+
NMP	+	+	+	+	+	+	+	+
DMSO	+	+	+	+	+	+	+	+
H ₂ SO ₄	+	+	+	+	+	±	+	±
MeOH	±	-	±	-	-	-	-	-
EtOH	-	-	-	-	-	-	-	-
CHCl ₃	-	-	-	-	-	-	-	-
CH ₂ Cl ₂	-	-	-	-	-	-	-	-
H ₂ O	-	-	-	-	-	-	-	-

Concentration: 5 mg ml^{-1} ; (+): soluble at room temperature, (-): insoluble, and (±): soluble with heating. DMAc: N,N-dimethyl acetamide; DMF: N,N-dimethyl formamide; NMP: N-methyl pyrrolidone; DMSO: dimethyl sulfoxide, MeOH: methanol, EtOH: ethanol

The inherent viscosity of the polymers was in range 0.18-0.49 dL/g. The results of measurements showed that the synthesized polyurethane from the same monomers specially, aromatic monomers, had a good average chain length growth. Increased viscosity results in increased molecular weight, and then improves physical properties and thermal properties.

Thermal properties of PU

Thermal properties of PEAs were evaluated with TGA and DTG under air atmosphere at a heating rate of 30 °C/min. Thermal stability of the polymers was evaluated based on T_0 (initial decomposition temperature), T_{10} (temperature for 10 % weight loss), T_{max} (maximum decomposition

temperature) and residues of the polymers at 600 °C (char yield).

High thermal stability of the polymers was concluded according to the TGA data. It could be mainly related to aromatic and rigid structure of monomers. Because of the higher rigidity and symmetry of TPC and HQ in comparison to the other polymers, the highest thermal stability data was related to it. PEAs containing aliphatic linkages (APC-EG-HDI and APC-EG-MDI) showed lowest thermal stability among the polymers due to the presence of weak aliphatic units in which reducing of thermal stability was intensified by increasing of aliphatic chains (APC-EG-HDI PU). However, its biodegradation seems more than the other PUs.

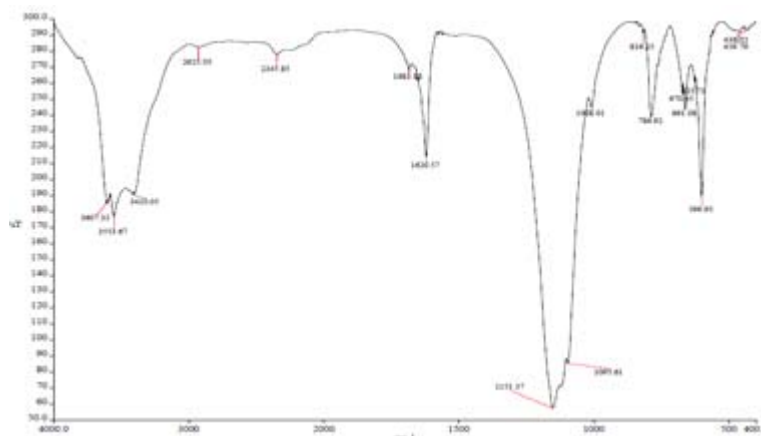


Fig. 1. FT-IR spectrum of optically active diacid based on APC

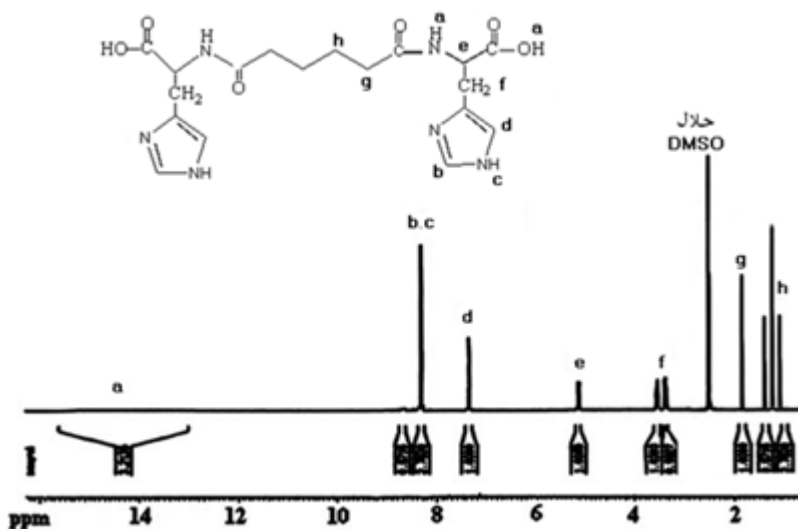


Fig. 2. $^1\text{H-NMR}$ spectrum of optically active diacid based on APC

All of the prepolymers and PUs showed optically active properties, and the specific rotations of PUs were measured in DMF at a concentration of 0.5 g/dL at 25°C in the range -43.28 to -80.3.

Characterization of nanocomposites

Although, all polyurethanes were synthesized and well characterized, their thermally stable, biocompatible, biodegradation and antibacterial were improved with preparing their related magnetic nanocomposites though introducing Fe_3O_4 in to polymer matrix. Among the PEAs, APC-EG-HDI PU selected due to the

appropriate growing polymer chain length then thermal stability properties and biodegradation ability. Magnetic nanoparticles (NPs) in a sonic bath were dispersed well in a solution of monomers. It is demonstrated that using ionic liquids (ILs) could help the NPs to disperse in polymer chains when they are forming by in-situ polymerization method. Good cooperation between organic and inorganic phases is one of the important roles of ILs in preparing of nanocomposites.

XRD and SEM images

According to the X-ray diffraction studies and SEM images, a good quality of

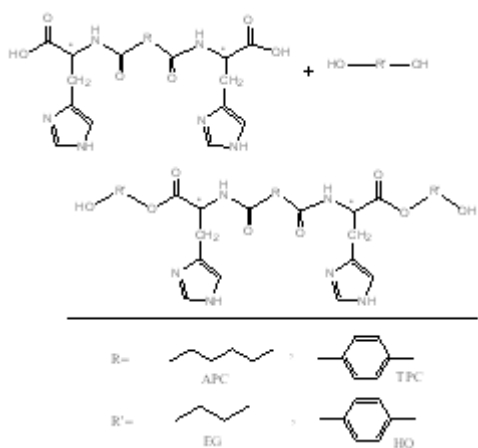


Fig. 3. Synthesis of polyester-polyols

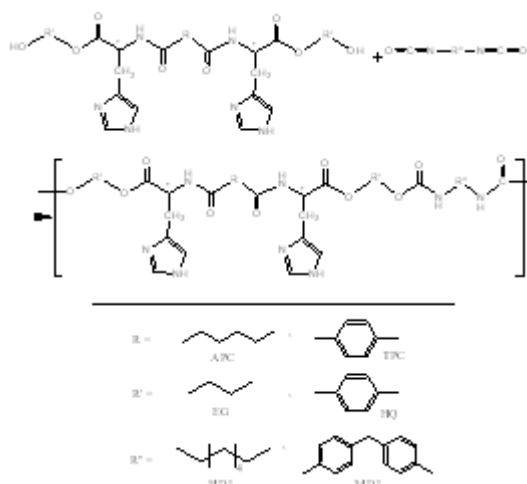


Fig. 4. Synthesis of poly(ester-amide-urethane)s

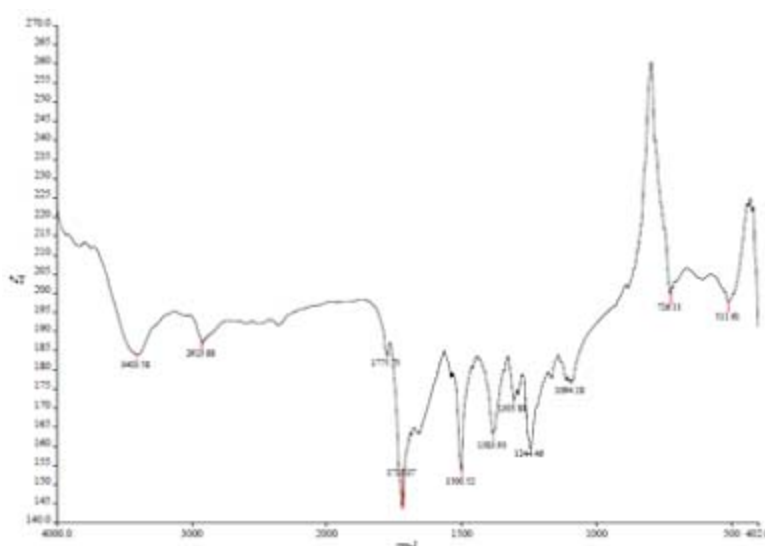


Fig. 5. FT-IR spectrum of optically active polyurethane (TPC-EG-HDI)

magnetic NPs and their good distribution of them in nanocomposites achieved due to good properties. The SEM images are illustrated in figure (6) show synthesis of Fe_3O_4 in nano scale and good distribution on matrix.

Thermally properties of nanocomposites

The results showed that thermal resistance of PUs was enhanced with adding more Fe_3O_4 NPs in composites. Preparation of a homogenous composite 30% wt. Fe_3O_4 was possible

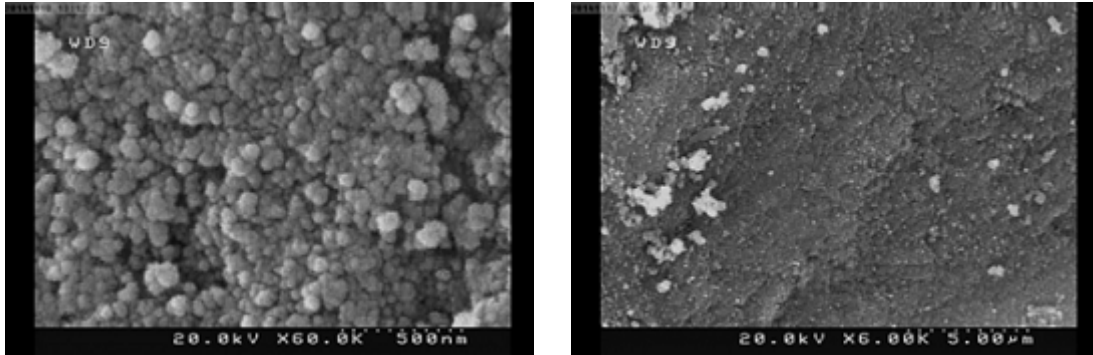


Fig. 6. SEM images of Fe_3O_4 NPs and composite

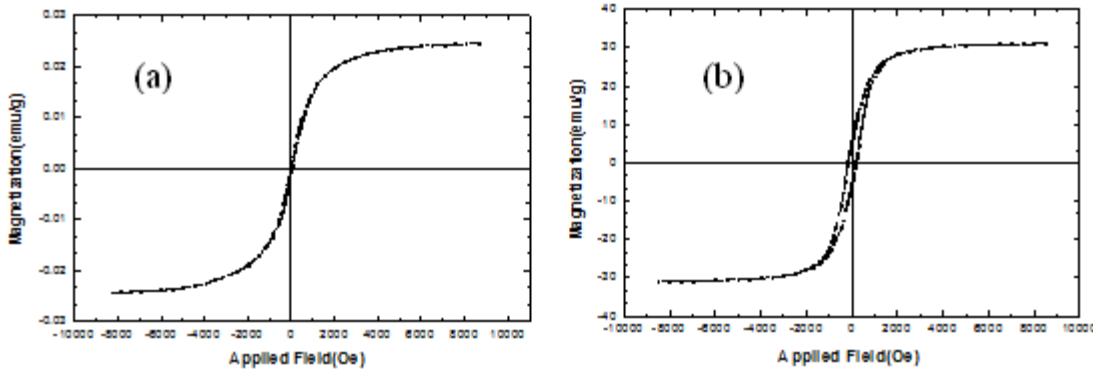


Fig. 7. Magnetic hysteresis loop of polymer (a) and PU/ Fe_3O_4 30% NCs (b)

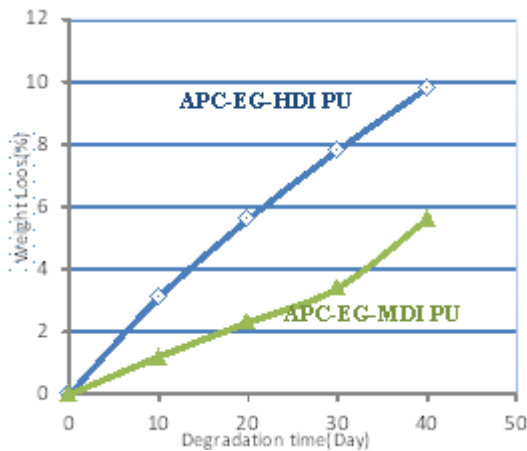


Fig. 8. Weight loss percentages of polyurethanes

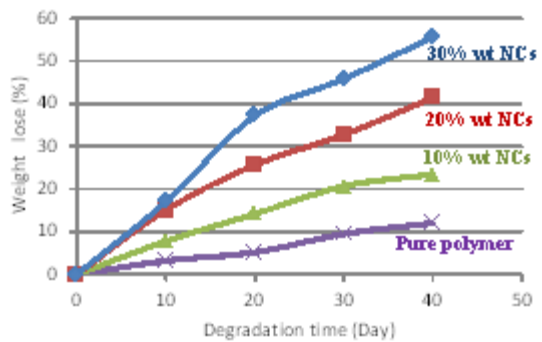


Fig. 9. Weight loss percentages of polyurethane/ Fe_3O_4 nanocomposites graphs

via using ethyl methyl imidazolium bromide as IL and a disperss agent. These ionic molecules with hydrogen bonds and polar-polar interaction cover the NPs to avoid agglomeration and make an uniform composite materials. Although increasing in size of NPs or agglomeration in nanocomposites, cause difficulties in thermal and mechanical properties. TGA curves for APC-EG-HDI PU were showed improving in thermal properties, with increasing NPs weight percentages. Thermal behaviors of polymers were investigated using DSC technique. Polyurethane with 30% wt of Fe_3O_4 , revealed highest and the pure PUs showed lowest glass transition temperature among the prepared polymer based nanocomposites. Also as it should be mention that, polymers obtained through IL method revealed higher thermal stability in comparison to the same nanocomposites obtained without any dispersing agent. It was attributed to the higher dipole-dipole interaction of polymer chains and backbones with NPs.

Magnetic properties

The magnetic Fe_3O_4 NPs are ferromagnetic. This substance in the absence of an external magnetic field has a spontaneous magnetization and unlike paramagnetism, their magnetic moments interact with themselves. It has magnetism and permanent magnet attract. The orientation of magnetization is in a direction completely.

Since the magnetic NPs spread in to the polymer, the magnetic properties of nanocomposites were enhanced. This property, compared with pure polymer through a conventional magnetic field by magnet. In this

experiment, the PU/ Fe_3O_4 nanocomposites drawn and attracted to the magnet more. It can be seen that with increasing magnetic NPs in the polyurethane matrix, composites tend to be more magnets. When the magnetic composite sample, is into magnetic field, magnetization increases fast. By increasing the applied magnetic field, magnetization increases acceleration decreases. This deceleration continues until its medium magnetization reach to Ms saturation. As magnetic hysteresis loop of pure PU (a) and PU/ Fe_3O_4 30% wt. NCs (b) are illustrated in Figure (7), magnetism can be increased compared to pure polymer substrate.

Biodegradation of polyurethane nanocomposites (PU-NCs)

Hydrolytic degradation of samples that include weight loss percentage of samples in phosphate-buffered saline (PBS) with respect to time was evaluated as a measure of the rate of biodegradation. The percentage of weight loss relative to the initial weight of the samples was calculated by the following formula:

$$\text{weight loss (\%)} = \frac{\text{The dry collected sample from the buffer solution}}{\text{The initial weight of the dry sample}}$$

However, thermal stability and mechanical strength of polyurethanes synthesized from fully aromatic monomers were not compatible with other polymers, optically active linkages in polyurethane backbone effects on more biodegradability. Among the synthesized polymers, APC-EG-HDI PU with optically active property, showed a good degradation compare to the others as it illustrated in figure (8). Anyway, presence of the aliphatic bonds in polymer chains causes the biodegradability. In addition, using some weight

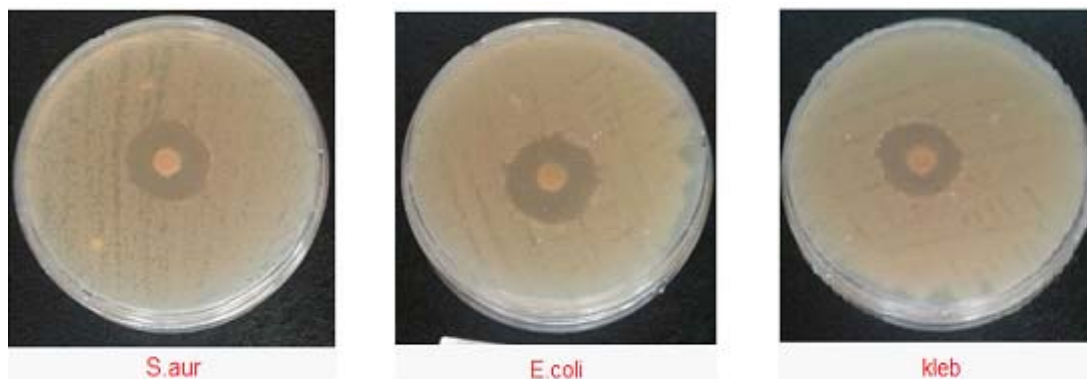


Fig. 10. Comparative antibacterial effect of optically active PU- Fe_3O_4 10 in presence of three pathogens; *S. aur*, *E. coli*, and *Kleb*

percentage of Fe_3O_4 magnetic nano particles in polymer matrix defenately accelerates its rate. This property will be more and more with gradual increasing the greater the amount of Fe_3O_4 into composite. The 30% wt. Fe_3O_4 PU composite showed more degradation rate than 20% wt., 10% wt. and 5% wt. of magnetic Fe_3O_4 nanoparticles in polymer matrix with more lose weight in the same time, respectively as it shown in figure (9).

Anti-bacterial properties

Anti-bacterial property is one of the significant properties in medical, food and packaging industries. It is demonstrated that most NPs have this feature. Hence, presence of the magnetic Fe_3O_4 NPs showed it. Anti-bacterial investigation was done with 5 types of pathogens; listeria mono-cytogenes Escherichia coli, Bacillus subtilis, Staphylococcus aureus, and Shigella dysentery. About 1.0 grams of the composites were used in this experiment.

Halo forming around the discs showed a broadly anti-bacterial and anti-bacterial absence of aura indicates a lack of this combination. The halo was engendered around the most samples with pathogens which proved their anti-bacterial feature (figure 10).

CONCLUSION

Novel polyurethanes containing optically active monomers were prepared using pre-polymer method. Introducing hydrolysable ester, optically active carbon, thermally stable amide, and bulky pendant imidazole units into the polymer backbone disturbed inherent macromolecular degradedly, inter-chain hydrogen bonding, packing efficiency that caused superior properties. In this way, ZVI nano-particles that were synthesized by co-precipitation method were isolated in the polymeric matrix. Using ionic liquid in preparation of nanocomposites was so effect on homogeneous distribution of NPs in polyurethane matrix. Hence, to increase weight percentages of Fe_3O_4 some properties such as thermally resistance, magnetic, optically active, biocompatibility, and biodegradability were gradually developed. The obtained composites showed appropriate biodegradation that was attributed to the bio nature of amino acid moieties, hydrolysable ester and urethane bonds and biocompatible magnetic NPs

simultaneously. Presence of Fe_3O_4 magnetic nanoparticles makes the anti-bacterial composites for using medical devices.

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