Biocompatible polyurethane/thiacalix[4]arenes **functionalized** Fe₃O₄ magnetic nanocomposites: synthesis and properties

Abbas Mohammadi ^a, Mehdi Barikani ^{b,*}, Moslem Mansour Lakouraj ^a

^a Department of Polymer Chemistry, University of Mazanadaran, P.O. Box 47416, Babolsar, Iran

^b Department of Polyurethane, Iran Polymers and Petrochemicals Institute, P.O. Box 14965-115, Tehran, Iran

Abstract

In this study, a series of magnetic polyurethane/Fe₃O₄ elastomer nanocomposites were prepared by covalently embedding novel thiacalix[4]arenes (TC4As) functionalized Fe₃O₄ nanoparticles (TC4As-Fe₃O₄) which contain macrocycles with reactive hydroxyl groups. Surface functionalization of Fe₃O₄ nanoparticles with TC4As macrocycles as unique reactive surface modifier not only gives specific characteristics to Fe₃O₄ nanoparticles but also improves the interphase interaction between nanoparticles and the polyurethane matrices through covalent attachment of polymer chains to nanoparticle surfaces. The novel synthesized TC4As-Fe₃O₄ nanoparticles were characterized by FTIR, XRD, TGA, VSM and SEM analysis. Furthermore, the effect of functionalization of Fe₃O₄ nanoparticles on the various properties of resulting nanocomposites was studied by XRD, TGA, DMTA, SEM, and a universal tensile tester. It was found that the functionalization of nanoparticles with TC4As affords better mechanical and thermal properties to polyurethane nanocomposites in comparison with unmodified nanoparticles. The SEM analysis showed finer dispersion of TC4As-Fe₃O₄ nanoparticles than unmodified Fe₃O₄ nanoparticles within the polyurethane matrices, which arising from formation of covalent bonding between TC4As functionalized Fe₃O₄ nanoparticles and polyurethane matrices. Moreover, the investigation of in vitro biocompatibility of novel nanocomposites showed that these samples are excellent candidate for biomedical use.

Keywords: Biocompatible polyurethane nanocomposites; Magnetic nanostructures; Surface functionalization; Thiacalix[4]arenes; thermo-mechanical properties.

*corresponding author

M.Barikani@ippi.ac.ir

Tel: +98 2148662427

Fax: +98 2148662020

1. Introduction

Polyurethanes (PUs) are a category of highly significant engineering polymers with excellent biocompatibility properties. Due to their easily modifiable structure, polyurethanes are used for various commercial applications in many areas, such as medical devices, coatings, adhesives, construction, automatic industries, sealants, and textiles industries [1-3]. Polyurethane elastomers (PUEs) are widely used because they can show interesting properties with a changing chemical structure of three starting constituents: a diisocyanate, a long-chain diol (or polyol) and a small molecule as chain extender [4]. Polyurethane elastomers are formed from soft segments and hard segments sequences. The soft segments are derived from the polyol, while hard segments are derived from a diisocyanate and a chain extender [5].

Magnetic nanoparticles, especially Fe_3O_4 nanoparticles have attracted much interest in various areas including magnetic recording, magnetic sensing, catalyst, drug delivery systems (DDS), magnetic resonance imaging (MRI), and cancer therapy [6]. The Fe_3O_4 magnetic nanoparticles tend to agglomerate due to large surface area to volume ratio and also magnetic dipole-dipole interaction between nanoparticles [7]. Significant efforts have been made toward the surface modification of magnetic nanoparticles with different strategies to avoid agglomeration in polymer matrices. Another advantage of surface modification is that the surface of Fe_3O_4 magnetic nanoparticles can be functionalized for specific applications such as, nanocomposites, catalysis, drug delivery, and efficient separation with the advantages of high dispersion, high reactivity, and easy separation [6]. A wide range of chemicals, such as polyacrylic acid, thiodiglycol, carboxymethyl- β -cyclodextrin and sodium alginate, have been used to functionalize and modify the surface of Fe_3O_4 magnetic nanoparticles to provide a better surface specificity for the desired application [8].

1 Incorporation of Fe_3O_4 magnetic nanoparticles into organic polymer matrices to fabricate
2 organic-inorganic nanocomposites has attracted considerable attention in many areas, such as
3 biomedical implants and devices, drug delivery, electromagnetic interference shielding (EMI),
4 water purification, magnetic shape memory polymers (MSMP) [9]. Polyurethane as organic
5 matrix is highly favored because of several advantages such as excellent mechanical properties,
6 chemical stability, blood and tissue compatibility and particularly, low cost products [10,11].

7 The most important problem in fabrication of organic-inorganic nanocomposites is to provide a
8 large area of interphase boundaries in nanocomposites. Interphase is an inhomogeneous area
9 between nanoparticles and a polymer matrix, which is affected by the surface properties of the
10 nanoparticles and the polymer matrix. However, proper surface modification of nanoparticles
11 could improve the interphase interaction and compatibility between the nanoparticles and
12 polymer matrices, which can further improve the quality of nanocomposites [12, 13].

13 Thiacalix[4]arenes (TC4As), as a new subclass of classical calixarenes, are macrocyclic
14 compounds possessing four phenol units linked by four bridging sulfur atoms instead of four
15 methylene bridging groups in the classical calix[4]arenes. The conic cavity shape, high thermal
16 stability, host-guest property and self-assembling nature of these macrocycles make them
17 attractive candidates in the fields of supramolecular chemistry, molecular detection and removal
18 of effluents [14-16]. Thus, the use of thiacalix[4]arenes derivatives in the backbone of
19 polyurethanes makes them a potential candidate for the adsorption of industrial effluents such as
20 heavy metals and dyes [17,18].

21 The present work describes fabrication of polyurethane/ Fe_3O_4 nanocomposites based on
22 thiacalix[4]arenes as novel reactive surface modifier on the surface of Fe_3O_4 magnetic
23 nanoparticles. The novel thiacalix[4]arenes functionalized Fe_3O_4 nanoparticles (TC4As- Fe_3O_4)

1 were firstly synthesized and then incorporated into polyurethane elastomers using in situ method
2 to prepare organic-inorganic polyurethane/Fe₃O₄ nanocomposites. It should be noted that surface
3 modification of Fe₃O₄ nanoparticles by thiacalix[4]arenes not only decrease the attraction forces
4 between nanoparticles and prevent agglomeration, but also improve the interphase interaction
5 between nanoparticles and the polyurethane matrix through covalent attachment of the polymer
6 chains to nanoparticle surfaces, which can further enhance the dispersion of nanoparticles within
7 polyurethane/Fe₃O₄ elastomer nanocomposites [19,20]. Moreover, considering excellent
8 intelligent structural and host-guest properties of TC4As, the produced polyurethane
9 nanocomposites can be good candidates for separation process as ion-exchange polyurethane
10 membranes.

11 To synthesize TC4As-Fe₃O₄ nanoparticles, the surface of the unmodified Fe₃O₄ nanoparticles
12 were firstly treated with 3-chloropropyltriethoxysilane (CPTMS) as silane coupling agent to
13 afford the CP-MNP nanoparticles and the obtained nanoparticles then were functionalized with
14 two thiacalix[4]arene derivatives (TC4As), namely *p-tert*-butylthiacalix[4]arene (*p*-BTC4A) and
15 tetrasodium thiacalix[4]arene tetrasulfonate (TSTC4AS).

16 The TC4As-Fe₃O₄ nanoparticles were characterized by Fourier transform infrared spectroscopy
17 (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), vibrating sample
18 Magnetometer (VSM) and scanning electron microscopy (SEM). The effects of the
19 functionalization of nanoparticles with TC4As on the various properties of the prepared
20 polyurethane nanocomposites were investigated and compared with pure polyurethane elastomer
21 and polyurethane nanocomposite incorporated with unmodified nanoparticles using ATR-FTIR
22 spectroscopy, TGA, dynamic mechanical thermal analysis (DMTA), XRD, SEM and a universal
23 tensile tester. The surface modification of Fe₃O₄ nanoparticles with thiacalix[4]arenes and

additional use of these magnetic nanoparticles to fabricate polyurethane/Fe₃O₄ elastomer nanocomposites has not, to the best of our knowledge, been previously explored.

2. Experimental

2.1 Materials

Poly (epsilon-caprolactone) diol (PCL) with molecular weight of 2000 g/mol was obtained from Solvay Chemicals Co. Hexamethylene diisocyanate (HDI) and 1,4-butanediol (1,4-BDO) were purchased from Merck. PCL and 1,4-BDO were dried at 70 °C under vacuum for 4h before use to ensure the removal of all air bubbles and water vapors that may otherwise interfere with the isocyanate reactions. Tetrahydrofuran (THF) as solvent was also distilled over sodium/benzophenone prior to use. All other chemicals used in the synthesis of unmodified and modified Fe₃O₄ nanoparticles are as follow: sulfur, *p-tert*-buthyl phenol, tetraethylene glycol dimethyl ether (tetraglyme), sodium hydroxide, and sulfuric acid, (3-chloropropyl) trimethoxysilane (97%), FeCl₂.4H₂O (Aldrich), FeCl₃.6H₂O (Aldrich), ammonium hydroxide, 25% (Merck).

2.2 Measurements

2.2.1 Characterization of nanoparticles

The structural properties of the synthesized nanoparticles were examined by X-ray diffraction (XRD) SIEMENS, D5000 X-ray diffractometer at room temperature. In order to confirm the surface functionalization of Fe₃O₄ nanoparticles, the compositions of the nanoparticles were examined in dried KBr powder by recording the infrared spectra over the range of 4000-400 cm⁻¹ using a Fourier transform infrared (FTIR) spectrophotometer (EQUINOX 55, Bruker Co). Magnetic properties of nanoparticles were also evaluated at room temperature with a vibrating sample magnetometer (VSM) made by Daghigh Kavir Corporation. The amount of reactive

surface modifiers on the surface of Fe_3O_4 nanoparticles was measured by a thermal analysis system, Perkin Elmer pyris 1. The dispersion and agglomeration tendency of the nanoparticles was also investigated by scanning electron microscope (SEM) using a Vega-II from TESCAN Co. Moreover, to disperse the Fe_3O_4 nanoparticles in THF, an ultrasonic homogenizer (SONOPULS HD 3200) was used. Transmission electron microscopic (TEM) image of the nanoparticles were obtained by a Philips CM 120 microscope. For TEM observation, powder samples were dispersed in ultra-pure water by sonication and were dropped onto a copper mesh. The hydrodynamic particle size and the particle size distribution of the nanoparticles were also measured by dynamic light scattering (DLS) using a laser diffraction (Malvern MasterSizer, UK) at 25 °C.

2.2.2 Characterization of prepared nanocomposites

Chemical structure of all the polyurethane samples was investigated by an attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. ATR-FTIR spectra were obtained with an EQUINOX 55, Bruker Co. All spectra were collected with 32 scans and at a resolution of 2 cm^{-1} over a wavenumber range of $4000\text{--}500\text{ cm}^{-1}$.

Thermogravimetric analyses (TGA) and derivative thermogravimetry (DTG) measurements were done on a thermal analysis system, Perkin Elmer pyris 1 under nitrogen and air atmosphere at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ from room temperature to $600\text{ }^\circ\text{C}$. The X-ray diffractograms of the prepared polyurethane samples were also obtained in a SIEMENS D-5000 X-ray diffractometer at room temperature with Cu anode radiation and wavelength of $1.5406\text{ \AA}$ generated at 35 kV and 25mA. The XRD spectra of the all samples were recorded with a scan rate of $1^\circ/\text{min}$ between $2\theta = 5^\circ$ and $2\theta = 35^\circ$.

The morphology and dispersion of the nanoparticles in polyurethane nanocomposites was evaluated with a scanning electron microscope (SEM) using a Vega-II from TESCAN Co. Samples were fractured in liquid nitrogen and covered with a gold layer to obtain better conductivity. The mechanical properties of the samples were also studied at room temperature with an Instron Model 1011 Universal Testing machine. A 1kN load cell was used and the crosshead speed was 50 mm/min. Pneumatic grips were used to hold the test specimens. Tensile tests were performed according to ASTM D 412 standard procedure. An average of three individual measurements was used for each sample.

The dynamic mechanical thermal analysis (DMTA) measurements were performed on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (Model MK-II) using tensile mode at a frequency of 1 Hz with a heating rate of 5 °C/min over a temperature range of -100 to 100 °C. Sample dimensions were 20 mm long, 10 mm width and 1 mm thickness.

Static and dynamic contact angle measurements were also implemented at room temperature via sessile drop method by a Kruss-G10 instrument. All the data presented were average of three measurements. The deionized water was used as medium to measure the contact angles.

2.3 Synthesis of thiacalix[4]arene derivatives

*2.3.1 Synthesis of *p*-tert-butylthiacalix[4]arene (*p*-BTC4A)*

p-BTC4A was prepared based on already reported method [14]. A mixture of *p*-tert-butylphenol (8 g), elemental sulfur S₈ (3.5 g), and NaOH (1.20 g) in tetraethylene glycol dimethyl ether (2.5 mL) was stirred under nitrogen. The stirred mixture was heated gradually to 230 °C over a period of 4 h and kept at this temperature for a further 3 h under nitrogen atmosphere. The obtained dark red mixture was cooled to room temperature and diluted with 35 mL of toluene and 50 mL of 4 M aqueous sulfuric acid solution, followed by addition of 50 mL of diethyl ether with

1 stirring to give a suspension. The precipitate was obtained by filtration, recrystallized from
2 ethanol and dried under vacuum at 100 °C for 2 h.

3 FT-IR (KBr, cm^{-1}): 3247(O–H), 2958 (C–H), 1559 (C=C), 1457 (C–H), 1196 (C–O) and 690
4 (C–S). ^1H NMR (400MHz, CDCl_3 , δ , ppm): 9.61 (s, 4H, OH), 7.56 (s, 8H, ArH), 1.24 (s, 36H, t-
5 Bu). ^{13}C NMR (400MHz, CDCl_3 , δ , ppm): 155.6, 144.7, 136.4, 120.5 (C, Ar), δ 34.2 (C, t-Bu), δ
6 31.2 (C, t-Bu).

7 2.3.2 Synthesis of tetrasodium thiocalix[4]arene tetrasulfonate (TSTC4AS)

8 TSTC4AS was synthesized based on the literature method [21]. At first, 1.5 g of *p*-BTC4A was
9 mixed with 80 mL of sulfuric acid (98%), and the suspension was heated at 80 °C for 4 h under
10 stirring. The solution was then cooled and poured into 500 mL of ice-cold water, and the
11 resulting purple solid was filtered. Then, 100 g of sodium chloride was added to the filtrate to
12 provide sodium salt. The obtained salt was dried and dissolved in 20 mL of water, and then
13 ethanol was added to form a milky precipitate. The white precipitate was filtered and dried in
14 vacuum oven at 90 °C for 4 h.

15 FT-IR (KBr, cm^{-1}): 3449 (O–H), 1182 and 1138 (S=O). ^1H NMR (400MHz, D_2O , δ , ppm): The
16 H of –OH disappeared on exchange with D_2O , 7.91 (s, 8H, ArH). ^{13}C NMR (400MHz, D_2O , δ ,
17 ppm): 160.81, 134.80, 134.28, 121.49.

18 2.4 Synthesis of unmodified Fe_3O_4 nanoparticles

19 Herein, unmodified Fe_3O_4 nanoparticles were prepared by coprecipitation method using FeCl_2
20 and FeCl_3 in 1:2 molar ratio [13]. In order to synthesize 2 g pure Fe_3O_4 nanoparticles (MNP),
21 4.68 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1.72 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 50 mL deionized water. The
22 resulted solution was deoxygenated by bubbling N_2 gas. Then, 10 mL of ammonium hydroxide
23 was added dropwise into the above solution under vigorous stirring and protection of dry N_2 gas

1 at 70°C. Further, the experiment was continued for 100 min. Precipitated black Fe₃O₄
2 nanoparticles were separated with a magnet. The precipitate was washed several times with
3 deionized water to remove excess materials. Hydrochloric acid (0.01M) was finally used to
4 neutralize the negative charge of nanoparticles. Finally, Fe₃O₄ nanoparticles were dried in
5 vacuum oven at 80 °C for 4 h.

6 **2.5 Synthesis of TC4As-Fe₃O₄ nanoparticles**

7 In order to enhance interphase interaction between the nanoparticles and polyurethane matrices,
8 the Fe₃O₄ nanoparticles were functionalized with thiacalix[4]arenes which contain reactive
9 hydroxyl groups as novel reactive surface modifiers. For this purpose, the Fe₃O₄ nanoparticles
10 were firstly treated by (3-chloropropyl) trimethoxysilane (CPTMS) as coupling agent to
11 introduce reactive chlorine groups onto the nanoparticles surface. Then, *p*-*tert*-butyl
12 thiacalix[4]arene (*p*-BTC4A) and tetrasodium thiacalix[4]arene tetrasulfonate (TSTC4AS) were
13 grafted onto the surface of modified Fe₃O₄ nanoparticles (CP-MNP) with one hydroxyl group of
14 macrocycles. TC4As functionalized Fe₃O₄ nanoparticles with reactive hydroxyl groups were
15 finally used for the next step in the preparation of polyurethane/Fe₃O₄ elastomer nanocomposites.
16 It should be mentioned that these functionalized nanoparticles can be embedded covalently in
17 polyurethane chains through reaction of their hydroxyl groups with NCO groups. The schematic
18 illustration of synthetic methods of TC4As functionalized nanoparticles can be seen in Figure 1.

19 *2.5.1 Synthesis of CPTMS modified Fe₃O₄ nanoparticles (CP-MNP)*

20 The surface of Fe₃O₄ nanoparticles was coated with CPTMS via Fe-O-Si bonds by a silanization
21 reaction to obtain CP-MNP nanoparticles. This was achieved by reaction of hydroxyl groups (-
22 OH) on the surface of unmodified Fe₃O₄ with the hydrolysable methoxy groups (-OCH₃) of
23 CPTMS. The reaction was carried out in a 250 mL three necked flask with a mechanical stirrer

as follows. 1.0 g of Fe_3O_4 nanoparticles was dispersed in 50 mL of toluene by mechanically stirring for 1 hour, and then 5 mL of CPTMS was added to the reaction mixture under continuous mechanical stirring. The reaction was allowed to proceed at 60 °C for 24 h under continuous stirring. The resultant CP-MNP nanoparticles were removed by magnetic separation with permanent magnet and were washed two times with dichloromethane and deionized water. The CPTMS modified Fe_3O_4 nanoparticles (CP-MNP) containing reactive chlorine groups were subsequently dried at room temperature under vacuum.

2.5.2 Synthesis of *p*-BTC4A functionalized Fe_3O_4 nanoparticles (TC-MNP)

A mixture of *p*-tert-butylcalix[4]arene (0.70 g) and potassium carbonate (0.07 g) in toluene (50 mL) was mechanically stirred for 30 min. Then, 1 g of CP-MNP was added to solution and reaction system was kept under mechanical stirring (1000 rpm) at 60 °C for 24 h. After magnetic separation, the resulted nanoparticles were washed with dichloromethane and water to remove excess unreacted compounds and also dried under vacuum.

2.5.3 Synthesis of TSTC4AS functionalized Fe_3O_4 nanoparticles (TS-MNP)

Herein, to attach tetrasodium thiacalix[4]arene tetrasulfonate onto the surface of the magnetic nanoparticles, the tetrasodium thiacalix[4]arene tetrasulfonate (0.80 g) and potassium carbonate (0.08 g) were mixed in 50 mL of dry NMP. In the second step, the CP-MNP nanoparticles (1.0 g) were added to the mixture under mechanically stirring (1000 rpm). The reaction was carried out under stirring at 60 °C for 24 h. The precipitate was separated by magnetic decantation and washed with dichloromethane and water and also dried under vacuum.

2.6 Synthesis of pure polyurethane elastomer

In this investigation, pure polyurethane elastomer (PUE) was synthesized using prepolymer method. At first, one equivalent of previously degassed poly (epsilon-caprolactone) diol (PCL)

and two equivalents of HDI were reacted at 90 °C for 3 h in a three-necked flask equipped with reflux condenser, mechanical stirrer, heating oil bath, dropping funnel, N₂ inlet and outlet to prepare NCO-terminated polyurethane prepolymer (NTP). The prepolymer was subsequently reacted with two equivalents of 1,4-butanediol as chain extender at 90 °C for 30 min and then obtained viscous polymer was poured into a Teflon mold and cured for 24 h in hot air circulating oven at 100 °C. Synthesis procedure of pure polyurethane elastomer is presented in detail in Figure 2.

2.7 Synthesis of polyurethane/Fe₃O₄ elastomer nanocomposites

Three different polyurethane/Fe₃O₄ elastomer nanocomposites were synthesized by embedding one weight percent of each MNP, TC-MNP and TS-MNP nanoparticles into polyurethane matrices through the in situ polymerization method in which polyol and diisocyanate are polymerized in presence of nanoparticles. Sample code designation and formulation of pure polyurethane and nanocomposites are given in Table 1. In order to fabricate nanocomposite, at first, a suitable amount of unmodified and functionalized nanoparticles were dispersed in 5 mL of THF by ultrasonic (sonication) homogenizing for 20 min at power of 40 W to produce a homogeneous dispersion of nanoparticles. Then, the dispersed nanoparticles were added to polyol by vigorous mechanical stirring (800 rpm) under nitrogen atmosphere at 90 °C in a three-necked flask equipped with reflux condenser, mechanical stirrer, heating oil bath, N₂ inlet and outlet. Afterward, polymerization reaction was carried out by adding a suitable amount of hexamethylene diisocyanate (HDI) to nanoparticles/polyol mixture under a nitrogen atmosphere at 90 °C for 3 h to form polyurethane prepolymer. The prepolymer was then mixed with a required amount of 1, 4-butanediol as chain extender with an equal ratio of NCO/OH at 90 °C for 30 min. The resulting viscous polymers were cast into a Teflon plate to form a uniform sheet of

1 1-2 mm thickness and then cured in oven at 100 °C for 24 h. The cured samples were maintained
2 for a week at ambient temperature for measurements and characterization.

3 **3. Results and Discussion**

4 Synthesis of thiacalix[4]arenes functionalized Fe_3O_4 nanoparticles (TC4As- Fe_3O_4) and
5 embedding them into polyurethane matrices to prepare polyurethane/ Fe_3O_4 elastomer
6 nanocomposites (MPUEs) using in situ polymerization method was investigated. It should be
7 mentioned that these functionalized nanoparticles can be embedded covalently in polyurethane
8 chains through reaction of their hydroxyl groups with NCO groups. Thus, surface
9 functionalization of Fe_3O_4 nanoparticles by thiacalix[4]arenes macrocycles containing reactive
10 hydroxyl groups not only decrease the attraction forces between nanoparticles and prevent
11 agglomeration, but also improve the interphase interaction between nanoparticles and the
12 polyurethane matrices through covalent bonding of the polymer chains to nanoparticle surfaces.

13 For synthesis of novel TC4As functionalized Fe_3O_4 nanoparticles (TC-MNP and TS-MNP) with
14 reactive hydroxyl groups, the surface of the unmodified Fe_3O_4 nanoparticles (MNP) were firstly
15 treated with 3-chloropropyltriethoxysilane (CPTMS) to afford the CP-MNP nanoparticles
16 containing reactive chlorine group, and afterward CP-MNP nanoparticles were functionalized
17 with two thiacalix[4]arenes macrocycles (TC4As) through covalent linkages.

18 The perfect synthesis of TC4As functionalized Fe_3O_4 nanoparticles was confirmed by FTIR,
19 XRD, TGA, VSM and SEM analysis. To prepare magnetic polyurethane/ Fe_3O_4 elastomer
20 nanocomposites (MPUEs), one equivalent of polyol in presence of a desired amount of
21 nanoparticles was reacted with two equivalents of HDI, and then obtained NCO-terminated
22 polyurethane prepolymer was subsequently extended with one equivalents of 1,4-BDO as
23 chain extender. The effects of the functionalization of Fe_3O_4 nanoparticles with TC4As on the

various properties of the prepared polyurethane/Fe₃O₄ elastomer nanocomposites were investigated and compared with both polyurethane nanocomposite incorporated with unmodified nanoparticles and pure polyurethane elastomer using ATR-FTIR spectroscopy, TGA, DMTA, XRD, SEM and a universal tensile tester.

3.1 Characterizations of nanoparticles

3.1.1 XRD study

The XRD patterns for the unmodified (MNP) and functionalized nanoparticles (TC-MNP and TS-MNP) are shown in Figure 3a. Six diffraction peaks presented by their indices (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) were observed for MNP, TC-MNP and TS-MNP nanoparticles. According to XRD patterns, the peak positions and relative intensities are in agreement with the XRD patterns of magnetic Fe₃O₄ nanoparticles in the literature [8]. Moreover, the results confirmed that the Fe₃O₄ nanoparticles are inverse spinel with a face-centered cubic (fcc) structure [22].

The crystallite mean size (D_c) of the nanoparticles can be determined using the Scherrer equation (Equation 1) [13]:

$$D_c = (k \lambda / \beta \cos \theta) \quad (1)$$

Where k is the shape function (a value of 0.89 is used), λ is the X-ray wavelength of the radiation, β is the full width at half maximum (FWHM) in radians of (311) peak in the 2θ scale, and θ is the diffraction angle. According to Scherrer equation, the D_c values for MNP, TC-MNP and TS-MNP are found to be 9.61 nm, 9.58 nm and 9.25 nm, respectively. It can be clearly seen from figure 3a that the peak intensities of TC-MNP and TS-MNP nanoparticles are lower than that of unmodified Fe₃O₄ nanoparticles. This observation can be assigned to presence of organic

shells (TC4As) on the surface of Fe_3O_4 nanoparticles. Moreover, TC-MNP nanoparticles with higher organic shell content showed weaker peak intensities compared to TS-MNP nanoparticles.

3.1.2 FTIR study

FTIR analysis was used to characterize the synthesized nanoparticles. Figure 3b shows the FTIR spectra of the MNP, TC-MNP and TS-MNP nanoparticles. For unmodified Fe_3O_4 nanoparticles (MNP), the intense band at 584 cm^{-1} can be assigned to the stretching vibration of Fe-O bonds. The broad and intense band at 3424 cm^{-1} can be attributed to the stretching vibration of surface hydroxyl groups of iron oxide. It should be pointed out that the band around 1628 cm^{-1} is attributed to the bending vibration of H-O-H linkage of water in the Fe_3O_4 nanoparticles [9, 24]. For the TC-MNP and TS-MNP nanoparticles, some new bands assignable to thiacalix[4]arene macrocycles on the surface of nanoparticles were also seen. FT-IR spectrum of TC-MNP presents two absorption bands at 588 and 628 cm^{-1} related to the Fe-O bonds in tetrahedral and octahedral respectively. Also, the band appearing at 3441 cm^{-1} can be attributed to stretching vibration of hydroxyl group which is originated from OH groups of *p*-BTC4A. Moreover, the stretching vibrations of Si-O bond at 1046 cm^{-1} , C-H stretching bands (2924 and 2857 cm^{-1}), C-H in plane bending (1155 and 1254 cm^{-1}), the O-H in plane and out of plane bands (1465 and 901 cm^{-1} respectively) and C=C vibration band of aromatic rings (1626 cm^{-1}) confirmed which TC4As are bounded on the surface of Fe_3O_4 particles. The significant features observed for TS-MNP are the appearance of vibration peaks at 1044 and 1129 cm^{-1} (S=O stretching), 990 cm^{-1} (Si-O stretching), 1638 cm^{-1} (C=C stretching), the O-H in plane and out of plane bands (1404 and 846 cm^{-1} respectively), and at 2922 and 2855 cm^{-1} (C-H stretching bands) [22, 25, 26]. All the above observations suggest that the surface of the Fe_3O_4 nanoparticles have been successfully functionalized with TSTC4AS.

3.1.3 TGA study

In order to investigate the amount of the surface modifier bounded onto the surface of Fe_3O_4 nanoparticles and achieve some information on thermal stability of synthesized nanoparticles, TGA analysis was carried out by heating nanoparticles under nitrogen at temperatures ranging from ambient temperature to 600 °C. TGA spectrum of synthesized nanoparticles is presented in Figure 4a. The trace weight loss of nanoparticles less than 150 °C can be assigned to desorption of adsorbed water on the surface of nanoparticles. Moreover, the weight losses above 150 °C are related to degradation of organic shells (CPTMS and TC4As) on the surface of Fe_3O_4 nanoparticles. In TGA curve of pure Fe_3O_4 , the second weight loss step can be attributed to dehydration of hydroxyl groups on the surface of Fe_3O_4 nanoparticles which formed in aqueous media synthesis [27]. In the TGA curve of CP-MNP nanoparticles, the amount of CPTMS bounded on the surface of the nanoparticles can be determined from the weight loss percentage of higher than 150 °C. It shows the mass loss percentage of CPTMS is about 7.2 %. For TC-MNP nanoparticles, two stages of weight loss were observed. About 7.2 % weight loss in the first stage (150–370 °C) is due to the loss of CPTMS and about 27.5 wt% weight loss can be assigned to thermal degradation of *p*-BTC4A on the surface of Fe_3O_4 nanoparticles in the second stage (370–600 °C). Furthermore, for TS-MNP nanoparticles, about 7.6 % weight loss in the first stage (150–370 °C) is due to the loss of CPTMS and about 20.1 wt% weight loss is attributed to thermal degradation of TSTC4AS in the second stage (370–600 °C). Moreover, the TC-MNP and TS-MNP nanoparticles contain 65.3 and 72.3 wt% inorganic Fe_3O_4 , respectively. The TGA results also suggest that the synthesized TC4As functionalized Fe_3O_4 nanoparticles are stable below 150 °C.

3.1.4 VSM study

The magnetic properties of the unmodified (MNP) and functionalized nanoparticles (TC-MNP and TS-MNP) were evaluated using VSM analysis at room temperature. The magnetization curves and magnetic parameters of the nanoparticles are presented in Figure 4b and Table 2. The result demonstrated that unmodified and functionalized nanoparticles have a superparamagnetic behavior at room temperature because of very insignificant coercivity (H_c) and remanent magnetization (M_r) in absence of external magnetic field [28]. It should be noted that superparamagnetism occurs when the particles are composed of very small crystallites (1-10 nm) and it is the responsiveness to an applied magnetic field without maintaining any magnetism after elimination of magnetic field [29]. TC-MNP and TS-MNP nanoparticles exhibited better superparamagnetic properties with lower H_c and M_r values compared to MNP nanoparticles. This observation can be ascribed to presence of organic shells on the surface of TC-MNP and TS-MNP nanoparticles which cause lower agglomeration tendency of these nanoparticles compared to pure Fe_3O_4 nanoparticles due to reduction in attractive forces between nanoparticles. The saturation magnetization (M_s) values of MNP, TC-MNP and TS-MNP are 57.02, 46.67 and 36.64 emu/g, respectively. This reduction in M_s values for TC-MNP and TS-MNP nanoparticles compared to pure Fe_3O_4 nanoparticles is due to non-magnetic behaviour of organic shells on the surface of Fe_3O_4 nanoparticles and is depending on the content of organic shells which were determined in TGA analysis [30, 31]. However, The TC-MNP nanoparticles containing higher amount of organic shell exhibited lower M_s value than that of pure Fe_3O_4 nanoparticles.

3.1.5 Dispersion stability of nanoparticles

The dispersion stability of pure and TC4As functionalized nanoparticles was investigated by monitoring the suspension and sedimentation of nanoparticles after 2 h, as captured in digital photographs (Figure 5). The all synthesized nanoparticles were dispersed (1.0 wt %) in water and

1 toluene via ultrasonic homogenizer for 20 min and the nanoparticles stability was studied after 2
2 h. As shown in Figure 5a, in water, the suspension stability of the CP-MNP and TC-MNP was
3 poor due to hydrophobic organic layer on the surface of these nanoparticles. In contrast, the TS-
4 MNP and MNP nanoparticles with hydrophilic surface exhibited exceptionally good
5 dispersibility in water, which forms a stable and uniform dispersion and no sedimentation was
6 observed after 2 h. As shown in Figure 5b, the functionalization of Fe_3O_4 nanoparticles with *p*-
7 BTC4A dramatically improved the dispersion stability of the TC-MNP in toluene which arises
8 from the hydrophobic nature of *p*-BTC4A on the surface of TC-MNP nanoparticles. Moreover,
9 MNP and TS-MNP nanoparticles indicated poor suspension stability with high sedimentation
10 after 2 h. This observation suggests that the presence of hydrophilic moieties on the surface of
11 Fe_3O_4 nanoparticles can increase the agglomeration tendency of MNP and TS-MNP
12 nanoparticles and thereby intensify the rate of nanoparticles sedimentation. Totally, the good
13 suspension stability of TC-MNP in toluene and also TS-MNP in water can be ascribed to
14 improvement in interfacial interaction between nanoparticles and solvents through
15 functionalization of Fe_3O_4 nanoparticles.

16 3.1.6 SEM analysis

17 SEM images of the unmodified and modified Fe_3O_4 nanoparticles are shown in Figure 6. In order
18 to prepare the samples for SEM analysis, 5 mg of nanoparticles were dispersed in 50 mL of THF
19 (as solvent for preparation of nanocomposites) using sonication for 20 min and were dropped
20 onto a clean glass slide and then dried under vacuum oven at 50 °C. As it can be seen from SEM
21 images, it is obvious that the CP-MNP and TC4As functionalized Fe_3O_4 nanoparticles (TC-MNP
22 and TS-MNP) are smaller and less agglomerated than unmodified Fe_3O_4 , while the unmodified
23 Fe_3O_4 nanoparticles are tightly joined together and form aggregates. This observation suggested

that the tendency of modified nanoparticles for aggregation is considerably reduced due to reduction in attractive forces between nanoparticles functionalization of the Fe_3O_4 nanoparticles with TC4As. TEM micrograph of the TS-MNP nanoparticles dispersed in water is shown in Figure 6. TEM image indicate that these nanoparticles are shaped from elliptical to sphere and roughly have an average size of 9.6 nm which is in good agreement with the crystallite mean size calculated from XRD analysis. According to TEM image, TS-MNP nanoparticles have a low degree of agglomeration due to reduction in attractive forces between nanoparticles by means of TSTC4AS bounded on the surface of Fe_3O_4 nanoparticles. The particle size distribution (expressed in number percent) of the TS-MNP nanoparticles is also shown in Figure 6. It is found that the particle size of TS-MNP nanoparticles obtained from DLS ranged from 36 to 120 nm with Z-average hydrodynamic particle size of 55.2 nm. This main difference between the measured particles sizes by both TEM and DLS techniques is due to the presence of an adsorbing layer, which is composed of TSTC4AS macrocycles on the surface of the Fe_3O_4 nanoparticle and solvent layer. It should be noted that organic compounds are electron transparent, and therefore, they did not show up in the TEM micrograph and only inorganic core is observable [32].

3.2 Characterizations of polyurethane/ Fe_3O_4 elastomer nanocomposites (MPUEs)

3.2.1 Structural characterization

Figure 7 shows the ATR-FTIR spectra of prepared pure polyurethane elastomer (PUE) and polyurethane/ Fe_3O_4 elastomer nanocomposites (MPUE, TC-MPUE and TS-MPUE). PUE sample was characterized with stretching vibrations of urethane N–H bond at 3329 cm^{-1} , stretching vibrations of urethane carbonyl at 1724 cm^{-1} asymmetric, and symmetric stretching vibrations of esteric carbonyl of PCL polyol at 1687 and 1661 cm^{-1} , respectively, and urethane N–H out-of-plane bending vibration at 1532 cm^{-1} . The C–H asymmetric and symmetric stretching vibrations

appeared at 2935 and 2863 cm^{-1} , respectively. The absorption bands at 1463 and 1363 cm^{-1} were assigned to CH_2 bending and CH_2 wagging vibrations, respectively. C–O–C asymmetric and symmetric stretching vibrations of PCL were observed at 1235 and 1158 cm^{-1} , respectively. The absorption bands at 1098 and 1043 cm^{-1} were also assigned to asymmetrical and symmetrical C–O–C stretching vibration of urethane groups [33, 34]. All of these IR spectra confirm the formation of a polyurethane structure. The asymmetric stretching vibration of the NCO group at 2270 cm^{-1} was used to determine the completeness of the reaction. There is no peak related to free isocyanate groups at approximately 2270 cm^{-1} , and this confirmed the complete reaction of isocyanate groups. The MPUEs (MPUE, TC-MPUE and TS-MPUE) also showed similar bands to PUE sample without significant shift in peaks position, which confirmed the completion of reaction. Furthermore, a slight shift in esteric carbonyl band position of TC-MPUE and TS-MPUE to higher wavenumber compared to PUE and MPUE was found. This shift in esteric carbonyl band position was attributed to decrease in hydrogen bonding between the urethane linkages in hard segments and esteric linkages in soft segments that can result from enhancement in microphase separation with embedding of TC4As functionalized nanoparticles into polymer chains. Moreover, it was observed that the characteristic urethane carbonyl peak of TC-MPUE and TS-MPUE shifted to lower wavenumber compared to PUE and MPUE which imply again the increase of microphase separation [5, 18].

3.2.2 Thermogravimetric properties

The thermal stability and decomposition behavior of the PUE, MPUE, TC-MPUE and TS-MPUE samples was evaluated by TGA and DTG analysis under nitrogen atmosphere. The TGA and DTG results are presented in Figure 8 and Table 3. Many investigations confirm that

polyurethanes are unstable at high temperature and depending on their constituents, thermal degradation reactions can take place during heating [35].

The thermal decomposition of all samples was evaluated at onset degradation temperature (T_{onset}) as a criterion for thermal stability, and also two different percentages of weight loss ($T_{10\%}$ and $T_{50\%}$). The decomposition of PUE sample starts at onset degradation temperature (T_{onset}) at 275 °C, which can be related to the depolymerization of urethane linkages. Moreover, for PUE sample, the temperatures with the mass loss of 10 and 50 % were found 318 and 338 °C. It was quite clear from TGA results that MPUE sample comprised from unmodified Fe_3O_4 nanoparticles (MNP) have lower T_{onset} , $T_{10\%}$ and $T_{50\%}$ than PUE sample. This lower thermal stability and decrease in T_{onset} , $T_{10\%}$ and $T_{50\%}$ for MPUE compared to PUE were attributed to disruption of hydrogen binding that is responsible for physical crosslinking between PU chains by unmodified Fe_3O_4 nanoparticles [36].

It is also obvious from TGA curve (Figure 8a) and Table 3 that the onset degradation temperature (T_{onset}) of TC-MPUE and TS-MPUE samples containing TC4As functionalized Fe_3O_4 nanoparticles is higher than that of PUE and MPUE samples and are more thermally stable. This occurs as a result of high thermal stability of thiacalix[4]arenes and also interfacial covalent bonding between the functionalized nanoparticles (TC-MNP and TS-MNP) and polyurethane matrices [37]. Moreover, in the case of TS-MPUE sample, lower thermal stability compared to TC-MPUE sample may be justified by repulsion forces between sulfonates groups of TSTC4AS macrocycle on the surface of nanoparticles imbedded into polyurethane chains. In addition, TGA analysis was also performed for TS-MPUE sample in air atmosphere to determine real residual inorganic Fe_3O_4 nanoparticles content in this nanocomposite (Figure 8c). Considering to Figure 8c, decomposition of TS-MPUE sample in air atmosphere begins at a

1 lower temperature than that of the nitrogen atmosphere. At 600 °C, the remaining Fe₃O₄
2 nanoparticles content for the TS-MPUE sample in air atmosphere was 0.75% which correlated
3 well with TGA result of TS-MNP nanoparticles containing 72 wt% of inorganic Fe₃O₄
4 nanoparticles.

5 The thermal degradation of polyurethane samples usually takes place in two main steps, the first
6 degradation step occurs from 200 to 350 °C and is related to the decomposition of the hard
7 segments, which encompasses the degradation of urethane linkages to polyol and isocyanate,
8 which then forms a primary amine, alkene, and carbon dioxide. The second main degradation
9 step occurs from 350 to 500 °C and is related to polyol degradation that can be impressed by
10 structure and morphology of the soft segments [38].

11 The DTG curves in Figure 8b clearly manifested that decomposition of polyurethanes samples
12 took place mainly in one step. This observation can be assigned to significantly higher degree of
13 microphase mixing due to high compatibility between PCL as polar soft segments and the polar
14 hard segments [39]. An inspection of the data in Table 3 indicates that the values of T_{max}
15 (temperatures with the maximum thermal degradation rate) in DTG curves decrease with
16 incorporation of nanoparticles into the polyurethane elastomers. However, the TC-MPUE sample
17 exhibits lower degradation rate and lower reduction in T_{max} compared to MPUE and TS-MPUE
18 samples.

19 3.2.3 Thermo-mechanical properties

20 Thermo-mechanical properties of the PUE and nanocomposites were studied by means of
21 dynamic mechanical thermal analysis (DMTA) which allows different kinds of transitions and
22 relaxations to be discerned [40]. The experiments were implemented in tensile mode as a

function of temperature from -100 to 100 °C and obtained results are presented in Figure 9 and Table 4.

Figure 9 shows the logarithm of storage modulus ($\text{Log } E'$) and dissipation factor ($\tan \delta$) as a function of temperature. It can be seen from storage modulus (Figure 9a) and loss tangent curves (Figure 9b) that all the samples show two thermal transitions which can be assigned to the thermal glass transitions (T_g) of soft segments in lower temperature and T_g of hard segments in higher temperature[41]. Furthermore, according to logarithm of storage modulus ($\text{Log } E'$) and loss of tangent curves, thermal glass transitions temperatures of polyurethane/ Fe_3O_4 elastomer nanocomposites (MPUE, TC-MPUE and TS-MPUE) occurred at higher temperature than PUE. This observation is due to reduction in mobility and free volume of polyurethane chains by incorporating nanoparticles into polyurethane matrices, and hence higher temperature is needed for increasing the chain mobility [34]. Table 4 reports the T_g values of soft segments and hard segments obtained from the $\tan \delta$ curves and also the $\text{Log } E'$ at temperature of 25 °C for PUE and prepared nanocomposites. In addition, $\tan \delta$ curves also showed that glass transition temperature (T_g) of TC-MPUE and TS-MPUE samples shifted to higher temperature compared to MPUE nanocomposite. This is because of the greater decrease in mobility of the polyurethane chains due to covalent bonding of TC-MNP and TS-MNP nanoparticles with polyurethane matrices through reactive hydroxyl groups of macrocycles on the surface of TC4As functionalized nanoparticles. According to Figure 9a, in the glassy and rubbery regions, module depression of TC-MPUE and TS-MPUE nanocomposite occurs in higher temperature as compared with PUE and MPUE nanocomposites, arising from good interaction between TC-MNP and TS-MNP nanoparticles and polyurethane matrices through covalent bond formation at interphase region.

3.2.4 SEM morphology

SEM microscopy was used to investigate the dispersion quality of nanoparticles in polyurethane matrices. SEM micrographs were gained through fractured cross section of the samples in liquid nitrogen (Figure 10). It is apparent from SEM images that unmodified Fe_3O_4 nanoparticles are tightly joined together and form aggregates, while the dispersion of TC-MNP and TS-MNP nanoparticles in polyurethane matrices is homogeneous and dramatically enhanced due to functionalization of Fe_3O_4 nanoparticles and thereby formation of covalent bonding between TC4As functionalized Fe_3O_4 nanoparticles and polyurethane matrices.

3.2.5 X-ray diffraction analysis

X-ray diffraction analysis was used to detect the crystalline state of the samples. Figure 11 shows the X-ray diffraction patterns for pure polyurethane and prepared nanocomposites. In polyurethanes, microphase separation or microphase mixing of soft segments and hard segments depends on their composition and structural order. All samples exhibited some broad and low height semicrystalline diffraction peaks at 2θ of 7.1, 20.2, 21.8 and 23.6 °, which implies the formation of a non-ordered structure because of microphase mixing. On the other hand, the diffraction peaks for TS-MPUE and TC-MPUE samples were more separated compared to PUE and MPUE samples. This observation suggests that the imbedding of TC-MNP and TS-MNP nanoparticles into polyurethane chains favor the formation of more ordered polyurethane structure owing to increase in microphase separation which was emphasized earlier by FTIR spectroscopy [42]. According to literature, XRD pattern for PCL polyol also shows two crystalline peaks at 2θ of 21.2 and 23.6 °. The observed peak positions for all samples are in good agreement with the XRD pattern of PCL (polyol). Thus, it is possible to say that observed peaks above 2θ of 15 ° for polyurethane samples are related to soft segments and also the broad

peak under 2θ of 10° can be ascribed to hard segments. However, XRD result clearly indicates that the all samples have semicrystalline hard and soft segments in amorphous medium [43, 44].

3.2.6 Mechanical behavior

The tensile stress-strain provides some useful mechanical parameters such as tensile strength, Young's modulus and elongation at break. The stress-strain curves of prepared PUE, MPUE, TC-MPUE and TS-MPUE samples are shown in Figure 12 and also the corresponding mechanical properties data are summarized in Table 5. The samples showed broad mechanical properties depending on the type of nanoparticles used.

In this part, mechanical properties are considered from the viewpoint of interaction quality of nanoparticles with polyurethane matrices. Functionalization of nanoparticles with TC4As macrocycles containing reactive hydroxyl groups was accompanied by an improved interfacial interaction between nanoparticles and polyurethane matrices and formation of suitable interphase region through covalent bonding. As confirmed earlier by FTIR and XRD analysis, functionalization of nanoparticles with TC4As macrocycles causes an increase in microphase separation degree and soft domain order in polyurethane nanocomposites.

All samples showed an elastic stress-strain behavior. The TC-MPUE sample showed higher tensile strength value compared to the other samples. This behavior is related to possibility of increase in crystallinity by drawing the sample, which arises from high degree of interphase interaction for this sample [43]. On the other hand, for MPUE sample with unmodified Fe_3O_4 nanoparticles exhibited poor tensile properties compared to PUE sample. This observation results from the poor interphase interaction between unmodified nanoparticles and polyurethane matrix, and thus a localization of shear stresses can appear at the negligible interphase region [45].

Moreover, the TS-MPUE showed significantly lower mechanical properties such as tensile strength and elongation at break compared to TC-MPUE sample. This behavior can be assigned to a considerable decrease in inter-chain forces due to the presence of anionic sulfonate groups (SO_3^-) of TSTC4AS on the surface of TS-MNP nanoparticles in polyurethane backbone which leads to electrostatic repulsion between chains and can reduce intermolecular forces in hard segments.

3.2.7 Wettability study

Investigation of the surface hydrophilicity of pure polyurethane elastomer (PUE) and polyurethane/ Fe_3O_4 elastomer nanocomposites was performed by water contact angle between water drops and the surface of the samples. The average values of obtained contact angles were reported as surface hydrophilicity of samples. The results showed that incorporation of unmodified Fe_3O_4 nanoparticles caused no significant change in contact angle of MPUE sample with 60.2° in comparison with PUE sample with contact angle of 59.3° . In addition, the contact angle of TC-MPUE increased to 71.7° with incorporation of TC-MNP nanoparticles, while with addition of TS-MNP, contact angle of TS-MPUE decreased to 41.2° . These results show that hydrophobicity of TC-MPUE samples increases with addition of TC-MNP nanoparticles due to hydrophobic nature of TC-MNP nanoparticles which was confirmed earlier in dispersion stability tests of nanoparticles in water and toluene solvents. It should be noted that the hydrophilicity of TS-MPUE is remarkably higher than PUE and MPUE samples. This can be explained by the fact that the sulfonate salt substitution attached to TSTC4AS on the surface of TS-MNP nanoparticles imparted more hydrophilic characteristics to TS-MPUE sample compared to PUE sample and other nanocomposites. Moreover, the advancing (θ_{adv}) and receding (θ_{rec}) contact angles and the corresponding hystereses for PUE and TS-MPUE samples

were calculated and are summarized in Table 6. Presence of hydrophilic TS-MNP nanoparticles in TS-MPUE nanocomposite increased its wettability as showed by the decreasing in θ_{adv} and θ_{rec} values. The contact angle hysteresis is a good criterion to assess the degree of surface roughness [46]. The increase in hysteresis value for TS-MPUE nanocomposite indicated that the addition of TS-MNP nanoparticles to polyurethane matrices increases the surface roughness.

3.2.8 Biocompatibility

Biocompatibility of fabricated nanocomposites was investigated by morphological evaluation of fibroblast cells after direct contact with nanocomposites. Mouse L929 fibroblast cells were precultured in 24-well plates using RPMI-1640 growth medium supplemented with 10 % fetal bovine serum at 37 °C and atmosphere of 5 % CO₂ for 24 h. The cells were then exposed to the sterilized samples, which placed in the center of each well and incubated at 37 °C for 24 h. A well containing cells and growth medium with no sample was set up as negative control. The cell growth characteristics and morphological changes were recorded using a Nikon te2000-u microscope. Figure 13 shows the optical microscopic images of the samples cultured with fibroblast cells. The original morphology of the fibroblasts before exposure to samples is represented in Figure 13a. Moreover, morphology of cells contacted with the PUE is shown in Figure 13b, while Figure 13c and 13d shows the cell proliferation after 24 h incubation with TC-MPUE and TS-MPUE nanocomposites. The evaluation of cell morphology for all samples showed cells survived and grew with spindle shape morphology and based on qualitative cell morphology assessment, the level of biocompatibility of samples are suitable [47].

4. Conclusions

In this work, a series of polyurethane/Fe₃O₄ elastomer nanocomposites were prepared via incorporation of thiacalix[4]arenes (TC4As) functionalized Fe₃O₄ nanoparticles (TC4As-Fe₃O₄)

1 into polyurethane matrices using in situ polymerization method. The TC4As macrocycles
2 containing reactive hydroxyl groups on the surface of nanoparticles can improve the dispersion
3 quality of the Fe_3O_4 nanoparticles within polyurethane matrices due to increase in interphase
4 interactions arising from formation of covalent bonding between nanoparticles and polymer
5 chains. The effects of the functionalization of nanoparticles with TC4As on the various
6 properties of the prepared polyurethane nanocomposites were investigated and compared with
7 both polyurethane nanocomposites incorporated with unmodified nanoparticles and pure
8 polyurethane elastomer using ATR-FTIR spectroscopy, TGA, dynamic DMTA, XRD, SEM and
9 a universal tensile tester. The enhanced and fine dispersion of the TC4As- Fe_3O_4 nanoparticles in
10 the nanocomposites were demonstrated by means of SEM analysis. It was also found that the
11 functionalization of nanoparticles with TC4As affords better mechanical and thermal properties
12 to polyurethane nanocomposites compared to unmodified nanoparticles. TGA results showed
13 that TC-MPUE and TS-MPE samples including TC4As functionalized Fe_3O_4 nanoparticles have
14 higher T_{onsets} than PUE and MPUE samples and are more thermally stable than the other samples.
15 In addition, $\tan \delta$ curves also showed that glass transition temperature (T_g) of TC-MPUE and TS-
16 MPUE samples shifted to higher temperature compared to MPUE nanocomposite. This is
17 because of greater decrease in mobility of the polyurethane chains due to covalent interaction of
18 TC-MNP and TS-MNPnanoparticles with polyurethane matrices. The surface hydrophilicity of
19 prepared samples was also investigated and the results endorsed the dependence of water contact
20 angle to the structure of thiacalix[4]arenes used on the surface functionalization of nanoparticles.
21 In addition, the investigation of in vitro biocompatibility of synthesized polyurethane elastomer
22 nanocomposites showed that these samples are excellent candidate for biomedical application.

Acknowledgment

The authors gratefully acknowledge the support of the University of Mazanadaran and financial support from the Iran National Science Foundation (INSF) under grant agreement No 92044523.

References

- [1] C. Hepburn, Polyurethane elastomers, Elsevier Applied Science, New York, USA, 1992.
- [2] K.M. Zia, F. Zia, M. Zuber, S. Rehman, M.N. Ahmad, Alginate based polyurethanes: A review of recent advances and perspective, *Int. J. Biol. Macromol.* 79 (2015) 377–387.
- [3] M.A. Hooda, B. Wanga, J.M. Sands, J.J. La Scala, F.L. Beyer, C.Y. Lia, Morphology control of segmented polyurethanes by crystallization of hard and soft segments, *Polymer*. 51 (2010) 2191–2198.
- [4] K. Kojio, T. Fukumaru, M. Furukawa, Highly softened polyurethane elastomer synthesized with novel 1, 2-bis (isocyanate) ethoxyethane, *Macromolecules*. 37 (2004) 3287–3291.
- [5] I. Yilgor, E. Yilgor, G.L. Wilkes, Critical parameters in designing segmented polyurethanes and their effect on morphology and properties: A comprehensive review, *Polymer*. 58 (2015) A1–A36.
- [6] A. Mohammadi, M. Barikani, Synthesis and characterization of superparamagnetic Fe₃O₄ nanoparticles coated with thiodiglycol, *Mater. Charact.* 90 (2014) 88–93.
- [7] W. Wu, Q. He, C. Jiang, Magnetic iron oxide nanoparticles: synthesis and surface functionalization strategies, *Nanoscale. Res. Lett.* 3 (2008) 397–415.
- [8] A. Mohammadi, H. Daemi, M. Barikani, Fast removal of malachite green dye using novel superparamagnetic sodium alginate-coated Fe₃O₄ nanoparticles, *Int. J. Biol. Macromol.* 69 (2014) 447–455.
- [9] A. Mohammadi, M. Barikani, M. Barmar, Effect of surface modification of Fe₃O₄ nanoparticles on thermal and mechanical properties of magnetic polyurethane elastomer nanocomposites, *J. Mat.Sci.* 48 (2013) 7493–7502.
- [10] H. Kalita, N. Karak, Hyperbranched polyurethane/Fe₃O₄ thermosetting nanocomposites as shape memory materials, *Polym. Bull.* 70 (2013) 2953–2965.
- [11] A. Mohammadi, M. Barikani, M. Barmar, Effect of polyol structure on the properties of the resultant magnetic polyurethane elastomer nanocomposites, *Polym. Adv. Technol.* 24 (2013) 978–985.
- [12] F. Mammeri, E. Le Bourhis, L. Rozes, C. Sanchez, Mechanical properties of hybrid organic–inorganic materials, *J. Mater. Chem.* 15 (2005) 3787–3811.
- [13] J. Lin, X. Wu, C. Zheng, P. Zhang, B. Huang, N. Guo, LY Jina, Synthesis and properties of epoxy-polyurethane/silica nanocomposites by a novel sol method and in-situ solution polymerization route, *Appl. Surf. Sci.* 303 (2014) 67–75.
- [14] N. Iki, C. Kabuto, T. Fukushima, H. Kumagai, H. Takeya, S. Miyanari, T. Miyashi, S. Miyano, Synthesis of p-tert-Butylthiacalix [4] arene and its Inclusion Property, *Tetrahedron*. 56 (2000) 1437–1443.
- [15] P. Lhoták, M. Himl, I. Stibor, H. Petříčková, Alkylation of thiacalix [4] arenes, *Tetrahedron. Lett.* 43 (2002) 9621–9624.
- [16] M.M. Lakouraj, F. Mojerlou, E.N. Zare, Nanogel and superparamagnetic nanocomposite based on sodium alginate for sorption of heavy metal ions, *Carbohydr. Polym.* 106 (2014) 34–41.

- [17] A. Mohammadi, M.M. Lakouraj, M. Barikani, Preparation and characterization of p-tert-butyl thiacalix [4] arene imbedded flexible polyurethane foam: An efficient novel cationic dye adsorbent, *React Funct. Polym.* 83 (2014) 14-23.
- [18] A. Mohammadi, M.M. Lakouraj, M. Barikani, Synthesis and investigation of properties of thiacalix[4]arene-based polyurethane elastomers, *Polym. Int.* 64 (2014) 421-429.
- [19] K.S. Wilson, A.J. Allen, N.R. Washburn, J.M. Antonucci, Interphase effects in dental nanocomposites investigated by small-angle neutron scattering, *J. Biomed. Mater. Res.* 81A (2007) 113–123.
- [20] D.L. Reid, R. Draper, D. Richardson, A. Demko, T. Allen, E.L. Petersen, S. Seal, In situ synthesis of polyurethane-TiO₂ nanocomposite and performance in solid propellants, *J. Mater. Chem. A.* 2 (2014) 2313-2322.
- [21] D. Yuan, W. X. Zhu, S. Ma, X. Yan, Bilayer structure of tetrasodium thiacalix [4] arene tetrasulfonate, *J Mol. Struct.* 616 (2002) 241-246.
- [22] L.G. Bach , M.R. Islam, J.T. Kim , S.Y. Seo , K.T. Lim, Encapsulation of Fe₃O₄ magnetic nanoparticles with poly(methyl methacrylate) via surface functionalized thiol-lactam initiated radical polymerization, *Appl. Surf. Sci.* 258 (2012) 2959–2966.
- [23] H.P. Klug, L.E. Alexander, X-ray diffraction procedures: for polycrystalline and amorphous materials, Wiley-Interscience, New York, 1974.
- [24] A.L. Willis, N.J. Turro, S. O'Brien, Spectroscopic characterization of the surface of iron oxide nanocrystals, *Chem. Mater.* 17 (2005) 5970-5975.
- [25] J. Safari, Z. Zarnegar, A magnetic nanoparticle supported Ni²⁺-containing ionic liquid as an efficient nanocatalyst for the synthesis of Hantzsch 1,4-dihydropyridines in a solvent-free dry-system, *RSC. Adv.* 3 (2013) 26094–26101.
- [26] B.H. Stuart, *Infrared Spectroscopy: Fundamentals and Applications*, John Wiley & Sons, New York, 2004.
- [27] A.R. Kiasat, S. Nazari, Magnetic nanoparticles grafted with β-cyclodextrin–polyurethane polymer as a novel nanomagnetic polymer brush catalyst for nucleophilic substitution reactions of benzyl halides in water, *J. Mol. Catal. A-Chem.* 365 (2012) 80-86.
- [28] R. Chantrell, J. Popplewell, S. Charles, Measurements of particle size distribution parameters in ferrofluids, *IEEE. Trans. Magn.* 14 (1978) 975-977.
- [29] A.Z.M. Badruddoza, G.S.S. Hazel, K. Hidajat, M.S. Uddin, Synthesis of carboxymethyl-β-cyclodextrin conjugated magnetic nano-adsorbent for removal of methylene blue, *Colloids and Surfaces A: Physicochem. Eng. Aspects.* 367 (2010) 85–95.
- [30] G. Goya, T. Berquo, F. Fonseca, M. Morales. Static and dynamic magnetic properties of spherical magnetite nanoparticles, *J. Appl. Phys.* 94 (2003) 3520-3528.
- [31] C.R. Lin, Y.M. Chu, S.C. Wang, Magnetic properties of magnetite nanoparticles prepared by mechanochemical reaction, *Matter. Lett.* 60 (2006) 447-450.
- [32] L. Zhang, R. He, H.C. Gu, Oleic acid coating on the monodisperse magnetite nanoparticles, *Appl. Surf. Sci.* 8 (2006) 2611–2617.

- [33] A. Mohammadi, M. Barikani, M. Barmar, Synthesis and investigation of thermal and mechanical properties of in situ prepared biocompatible Fe₃O₄/polyurethane elastomer nanocomposites, *Polym. Bull.* 72 (2015) 219-234.
- [34] Z. Chang, M. Zhang, A.G. Hudson, E.B. Orler, R.B. Moore, G. L. Wilkes, S.R. Turner, Synthesis and properties of segmented polyurethanes with triptycene units in the hard segment, *Polymer*. 54 (2013) 6910-6917.
- [35] Eceiza, M. Martin, K.D.L. Caba, G. Kortaberria, N. Gabilondo, M. Corcuera, I. Mondragon, Thermoplastic polyurethane elastomers based on polycarbonate diols with different soft segment molecular weight and chemical structure: Mechanical and thermal properties, *Polym. Eng. Sci.* 48 (2008) 297-306.
- [36] M. Ashjari, A.R. Mahdavian, N.G. Ebrahimi, Y. Mosleh, Efficient Dispersion of Magnetite Nanoparticles in the Polyurethane Matrix Through Solution Mixing and Investigation of the Nanocomposite Properties, *J. Inorg. Organomet. Polym. Mater.* 20 (2010) 213-219.
- [37] A. Saponar, E.J. Popovici, I. Perhaita, G. Nemes, A.I Cadis, Thermal behaviour of some ester derivatives of p-tert-butyl calix[n]arene, *J. Therm. Anal. Calorim.* 110 (2012) 349-356.
- [38] Q. Gong, J. Wu, X. Gong, Y. Fan, H. Xia, Smart polyurethane foam with magnetic field controlled modulus and anisotropic compression property, *RSC. Adv*, 3 (2013) 3241-3248.
- [39] A.K. Bhowmick, H. Stephens, *Handbook of elastomers*, CRC Press, Boca Raton, 2000.
- [40] K. Menard, *Dynamic mechanical analysis: a practical introduction*, CRC Press, Boca Raton, 1999.
- [41] P. Cinelli, I. Anguillesi, A. Lazzeri, Green synthesis of flexible polyurethane foams from liquefied lignin, *Euro. Polym. J.* 49 (2013) 1174-1184.
- [42] K.M Zia, I.A. Bhatti, M. Barikani, M. Zuber, H.N. Bhatti, XRD studies of polyurethane elastomers based on chitin/1,4-butane diol blends, *Carbohydr. Polym.* 76 (2009)183-187.
- [43] J. Kloss, M. Munaro, G.P. De Souza, J.V. Gulmine, S.H. Wang, S. Zawadzki, L. Akcelrud, Poly (ester urethane)s with polycaprolactone soft segments: A morphological study, *J. Polym. Sci. Part A: Polym. Chem.* 40 (2002) 4117-4130.
- [44] T. LaShanda. J. Korley, B.D. Pate, E.L. Thomas, P.T. Hammond, Effect of the degree of soft and hard segment ordering on the morphology and mechanical behavior of semicrystalline segmented polyurethanes, *Polymer*. 47 (2006) 3073–3082.
- [45] D.J. Martin, G.F Meijs, P.A. Gunatillake, S.J. McCarthy, GM. Renwick, The effect of average soft segment length on morphology and properties of a series of polyurethane elastomers. II. SAXS-DSC annealing study, *J. Appl. Polym. Sci.* 64 (1997) 803-817.
- [46] Q. Wei, D. Tao, Z. Du, Y. Cai, N. Wu, L. Chen, Surface nanostructures and dynamic contact angles of functionalized poly (ethylene terephthalate) fibers, *J. Appl. Polym. Sci.* 109 (2008) 654-658.
- [47] K.M. Zia, M. Zuber, I.A. Bhatti, M. Barikani, M.A. Sheikh, Evaluation of biocompatibility and mechanical behavior of polyurethane elastomers based on chitin/1,4-butane diol blends, *Int. J. Biol. Macromol.* 44 (2009) 18–22.

Figure captions

- Fig. 1** The schematic illustration of synthesis methods of TC4As functionalized Fe_3O_4 nanoparticles
- Fig. 2** Synthesis procedure of pure polyurethane elastomer (PUE)
- Fig. 3** X-ray diffraction (a) and FTIR spectra of synthesized nanoparticles (b)
- Fig. 4** TGA spectrum (a) and VSM magnetization curves of synthesized nanoparticles (b)
- Fig. 5** Dispersion stability investigation of synthesized nanoparticles in water (a) and toluene (b)
- Fig. 6** SEM and TEM images of synthesized nanoparticles and DLS result of TS-MNP nanoparticles
- Fig. 7** FTIR spectra of pure PU and nanocomposites
- Fig. 8** TGA (a) and DTG (b) thermograms of the pure PU and nanocomposites in nitrogen and TGA thermogram of TS-MPUE nanocomposite in air (c)
- Fig. 9** Logarithm of storage modulus (a) and $\tan \delta$ (b) curves of pure PU and nanocomposites
- Fig. 10** SEM images of PUE (a), MPUE (b), TC-MPUE (c) and TS-MPUE (d)
- Fig. 11** X-ray diffraction of pure PU and nanocomposites
- Fig. 12** Stress–strain curves of pure PU and nanocomposites
- Fig. 13** Optical microscopic images of the nanocomposites cultured with fibroblast cells; Negative control (a), PUE (b), TC-MPUE (c) and TS-MPUE (d).

Table captions

- Table. 1** Sample code designation and formulation of pure PU and nanocomposites
- Table. 2** Magnetic parameters of synthesized nanoparticles
- Table. 3** Thermal properties of pure PU and nanocomposites
- Table. 4** Thermal glass transition and storage modulus of pure PU and nanocomposites
- Table. 5** Mechanical properties results of pure PU and nanocomposites
- Table. 6** Advancing and receding contact angle values and corresponding hystereses

Tables

Table 1. Sample code designation and formulation of pure PU and nanocomposites

Sample code	Block ratio ^a (CAPA 225:HDI:BDO)	Nanoparticles type	Nanoparticle content (wt %)
PUE	1:2:1	None	0
MPUE	1:2:1	MNP ^b	1
TC-MPUE	1:2:1	TC-MNP ^c	1
TS-MPUE	1:2:1	TS-MNP ^d	1

^a Molar ratio of polyol: diisocyanate: chain extender

^b Fe₃O₄ magnetic nanoparticles

^c *p-tert*-butyl thiacalix[4]arene surface modified Fe₃O₄ nanoparticles

^d tetra-sodium thiacalix[4]arene tetrasulfonate surface modified Fe₃O₄ nanoparticles

Table 2. Magnetic parameters of synthesized nanoparticles

Sample	M _s (emu /g) ^b	H _c (Oe) ^c	M _r (emu /g) ^d	χ _i ^a
MNP	57.02	2.83	0.31	0.106
TC-MNP	46.67	2.12	0.21	0.109
TS-MNP	36.64	2.41	0.24	0.096

^a Magnetic susceptibility(the degree of magnetization of nanoparticles in response to applied magnetic field)

^b Saturation magnetization (the maximum possible magnetization)

^c Coercivity (the intensity of the applied magnetic field required to reduce the magnetization of nanoparticles to zero)

^d Remanent magnetization (the magnetization left in nanoparticles when external magnetic field is removed)

Table 3. Thermal properties of pure PU and nanocomposites

Sample code	T _{onset} (°C) ^a	T _{10%} (°C) ^b	T _{50%} (°C) ^c	T _{max} (°C) ^d
PUE	275	318	338	341
MPUE	270	307	332	335
TC-MPUE	293	315	334	340
TS-MPUE	283	315	337	335

^a Onset degradation temperature (temperature at which polymer degradation starts)^b Temperature at 10% weight loss^c Temperature at 50% weight loss^d Temperatures with the maximum thermal degradation rate**Table 4.** Thermal glass transition and storage modulus of pure PU and nanocomposites

Samples	T _{g,SS} (°C) ^a	T _{g,HS} (°C) ^a	LogE' (at 25 °C)
PUE	-45.1	6.1	7.69
MPUE	-44.2	6.8	7.54
TC-MPUE	-40.1	18.2	7.76
TS-MPUE	-37.6	19.2	7.92

^a Glass transition temperature of soft segment^b Glass transition temperature of hard segment

1 **Table 5.** Mechanical properties results of pure PU and nanocomposites

Sample code	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
PUE	11.10 ± 0.74	28.75 ± 0.31	519 ± 14
MPUE	8.14 ± 0.22	26.50 ± 0.45	405 ± 11
TC-MPUE	12.71 ± 0.43	16.12 ± 0.12	843 ± 21
TS-MPUE	7.25 ± 0.12	26.75 ± 0.38	578 ± 19

2

3

4

5 **Table 6.** Advancing and receding contact angle values and corresponding hystereses

Sample code	θ_{adv} (degree)	θ_{rec} (degree)	hysteresis
PUE	73.25	59.10	14.15
TS-MPUE	62.08	42.72	19.33

6

7

1

2

1

2

1

2

1

2

1

2

1

2

1

2

1

2

1

2

1

2

1