

Thermoresponsive surface functionalization of FeRh alloy through PNIPAM grafting

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Abstract

The smart thermoresponsive composite of PNIPAM/FeRh by chemical grafting of PNIPAM polymer on substrate of FeRh alloy were fabricated and studied. The characteristic peaks at 1690 (C=O), 2480–3000 (CH), and 3280 (N–H) observed on IR-FTIR spectra of PNIPAM/FeRh corresponded to the functional groups of PNIPAM and confirmed grafting of the polymer on the surface of FeRh substrate. The measurements of wetting demonstrated the changes of contact wetting angle from $69.3 \pm 1.5^\circ$ at 27°C to $76.9 \pm 1.2^\circ$ at 40°C attributed with transformation of PNIPAM polymer from the hydrated to the dehydrated state due phase transition with lower critical temperature at $\sim 32^\circ\text{C}$. The changes in surface topography of PNIPAM polymer in results of phase transition with lower critical solution temperature in PNIPAM were observed using atomic force microscopy measurements in temperature range $30\text{--}50^\circ\text{C}$ in heating and cooling.

Keywords

smart composites, polymer coating, surface modification, thermoresponsive polymers, PNIPAM, magnetocaloric effect, FeRh, FeRh alloys, functional magnetic materials

1. Introduction

"Smart" polymer composites are considered promising materials for biomedical applications due to their ability to significantly change their physicochemical properties under the influence of various external stimuli (temperature, pH, light) [1]. One of the polymers being actively investigated at present are thermosensitive polymers with a lower critical solution temperature (LCST), which

change their properties significantly with temperature change [2]. One of the well-known and most common thermosensitive polymers is poly (N-isopropylacrylamide (PNIPAM)), which in aqueous solution upon heating at $\sim 32^\circ\text{C}$ exhibits an LCST transition that reversibly changes from a swollen hydrated state to a wrinkled dehydrated state and loses about 90% of its volume. PNIPAM is a biocompatible polymer due to its proximity to physiological temperatures, which makes it a suitable material for various biomedical applications (drug delivery systems,

tissue engineering, smart coatings, etc.) [3–5]. PNIPAM can be used to create smart drug carriers that release active ingredients in response to changes in body temperature or environmental conditions. The polymer can also serve as a matrix for cell growth, providing conditions for tissue regeneration [6]. Its temperature-sensitive properties allow controlling the interaction of cells with the matrix. PNIPAM can be used to create coatings that change their properties depending on temperature, which can be useful in various medical applications [7, 8].

There are various ways of controlling the state of the thermosensitive polymer, from conventional heating to the use of a thermoelectric device [9, 10]. As a non-invasive way to control the properties of thermosensitive polymers, a new method for fabricating of 'smart' coatings for implants has been proposed in which the properties of thermosensitive polymers are controlled through magnetocaloric effect (MCE), and the binary FeRh alloy ordered to a CsCl-type structure has been proposed as one of the test magnetocaloric material, which exhibits a "giant" inverse MCE in the physiological temperature region [11–13]. The method of controlling the state of PNIPAM through inverse MCE in the case of FeRh is based on the fact that a single exposure to magnetic field of ~2 T cools the PNIPAM from ~37 °C to <32 °C and transforms PNIPAM from the shrunken dehydrated to the swollen hydrated state, which can be used for drug release [14]. The workability of this concept has been demonstrated using *in situ* experiments in magnetic fields up to 8 T [15], and also, the possibility of doxorubicin drug release loaded to PNIPAM/FeRh composite by applying of 3 T magnetic field was demonstrated [16].

However, one of the main disadvantages in these experiments was the detachment of the polymer from

the FeRh substrate under cyclic magnetic field effects, which was coated on the basis of physical coating methods, namely casting from the polymer melt. The aim of the present work is to search for new methods of surface functionalization with PNIPAM polymer based on chemical methods that allow to cross-link the polymer to the FeRh surface and exclude the problem of its detachment.

2. Methods and materials

2.1 Synthesis Fe₄₉Rh₅₁ material

The initial alloy Fe₄₉Rh₅₁ was obtained by arc melting of pure elements Fe (99.98%) and Rh (99.8%) in helium atmosphere (10⁻⁴ mbar), followed by annealing and quenching at 1000 °C for 7 days and quenching in air. The structure, magnetic, and magnetocaloric properties of this sample have been studied in detail in the works of [17, 18]. For the following treatment, the FeRh plate sized 4.5×3.5×0.2 mm was polished and cleaned in an ultrasonic bath to remove byproducts from the surface.

2.2. Surface modification of Fe₄₉Rh₅₁ plate by PNIPAM polymer

The PNIPAM/FeRh composite was obtained by chemical modification of the surface sample (FeRh plate) according to the following protocol. 0.05 mmol of PNIPAM-NH₂ (M = 2500 g/mol) was dissolved in 0.5 mL of DMF, and 0.05 mL of 0.5 M NHS-DTDP solution was added. After 30 min, 0.1 mL of solution was withdrawn

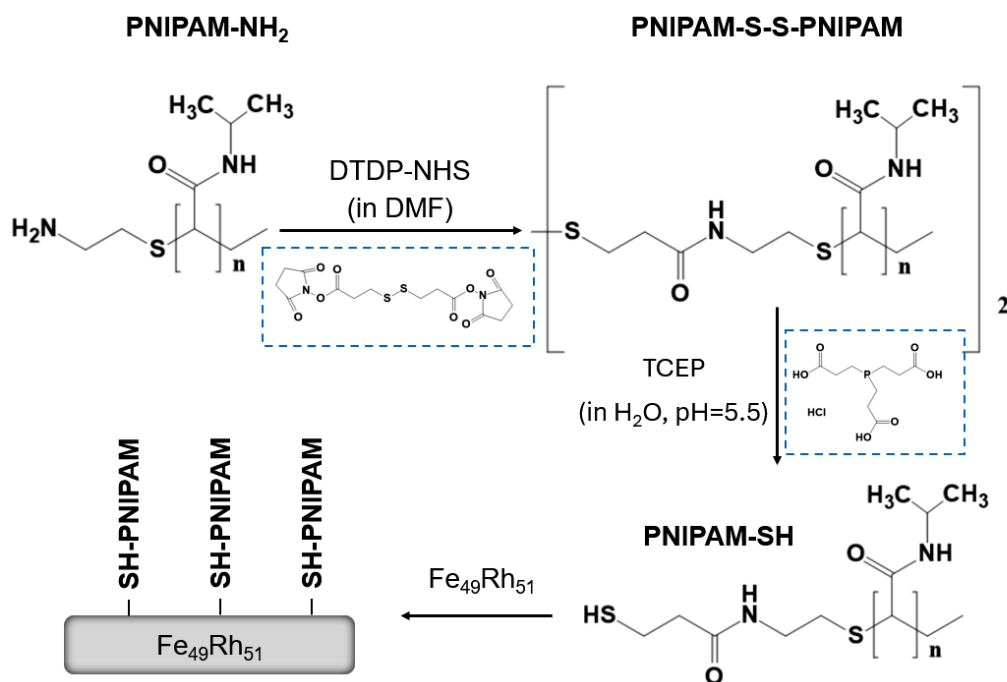


Figure 1. Scheme of surface functionalization of Fe₄₉Rh₅₁ by PNIPAM polymer

and diluted 10-fold with acetate buffer at pH = 5.5 with C = 0.1 M to 1 mL (0.1 mL conjugate + 0.1 mL 1 M buffer + 0.8 mL water). C(PNIPAM) = 10 mM. Next, 0.1 mL of 0.5 M TCEP solution is injected.

The resulting solution is poured onto the FeRh plate and left for 12 h. Then the plate is removed and washed twice with ethanol. The scheme of the procedure of FeRh surface functionalization with thermosensitive polymer PNIPAM is shown in Fig. 1.

2.3. Characterization

The chemical characterization of samples was performed by FTIR spectroscopy using multiple disturbed total internal reflection (MNTR) equipment. FTIR spectra (100 scans) were recorded in increments of 4 cm⁻¹ on a Vertex 80v FTIR spectrophotometer (Bruker). The spectra were collected at a pressure of 250 Pa at room temperature (20–25 °C) at an incidence angle of 45 deg.

The samples wettability was estimated by measuring the water contact angle (WCA). The measurements were carried out on an Easy Drop Kruss (KRÜSS, Germany) device. For each sample at least five WCA measurements were performed.

The surface morphology and its change under the influence of temperature were studied by scanning probe microscopy using a Ntegra Prima microscope (NT-MDT SI, Zelenograd, Russia). A special thermally insulated chamber was used for temperature measurements.

3. Results and discussion

FTIR spectra of FeRh and PNIPAM/FeRh are shown in Fig. 2a. The uncoated sample of FeRh is characterized by peaks which correspond to Fe–O [19] and Rh_xO_y [20, 21] contributions.

To assess surface changes, the spectrum of Fe₄₉Rh₅₁ was taken as a baseline to identify peaks that appeared after PNIPAM modification. The observed characteristic peaks at 1690 (C=O), 2480–3000 (CH), and 3280 (N–H) correspond to the functional groups of PNIPAM and suggest the ‘crosslinking’ of the polymer to the FeRh surface. The low intensity of the characteristic peaks can be associated primarily with the small amount of polymer on the surface.

One of the macroscopic phenomena characteristic of the temperature-sensitive polymer PNIPAM is the change of its wetting edge angle at the transition associated with LSCT as a result of temperature change [22]. Figure 2b shows images of contact angle measurements of pure Fe₄₉Rh₅₁ and PNIPAM-coated Fe₄₉Rh₅₁ at different temperatures.

As the measurements show, the transition from the hydrated to the dehydrated state leads to an increase in the wetting angle from an average value of 69.3±1.5 to 76.9±1.2 degrees that good correlates with the literature data [23]. The change in the wettability of PNIPAM as a result of the phase transition with LCST is one indirect evidence of successful chemical “crosslinking” of the polymer on the FeRh surface.

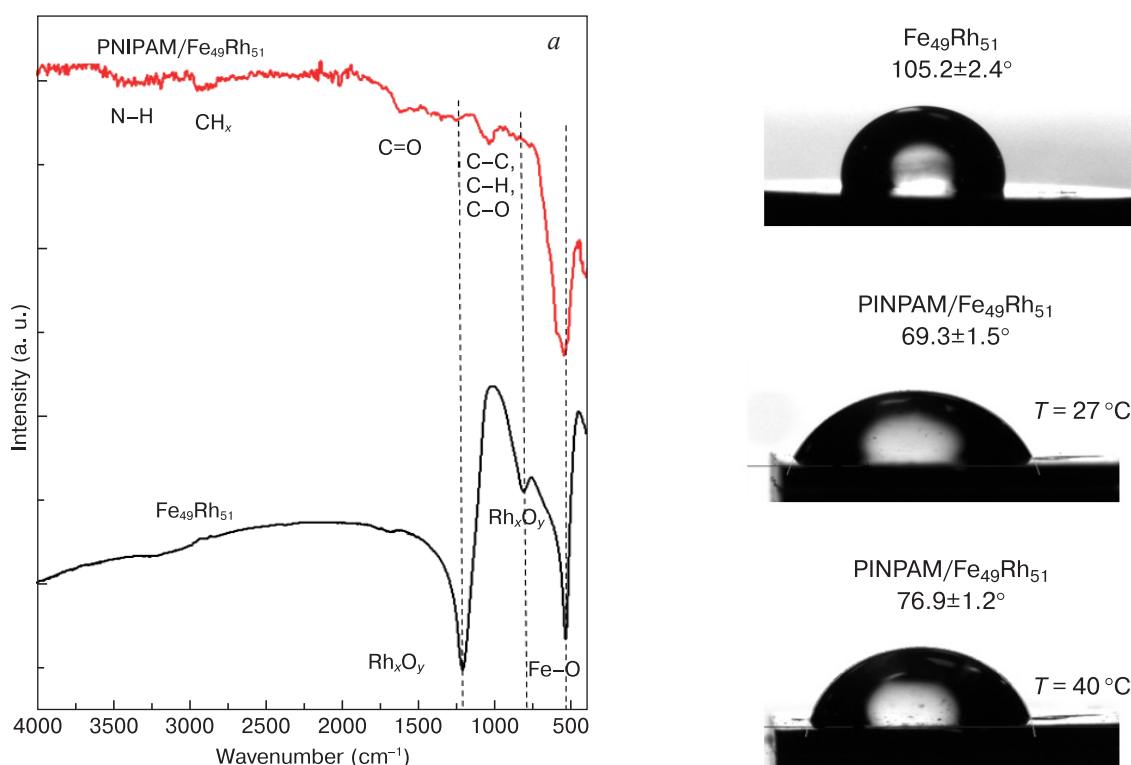


Figure 2. FTIR spectra of initial Fe₄₉Rh₅₁ and PNIPAM-coated Fe₄₉Rh₅₁ (a); water contact angle of initial Fe₄₉Rh₅₁ and PNIPAM-coated Fe₄₉Rh₅₁ at different temperatures (b)

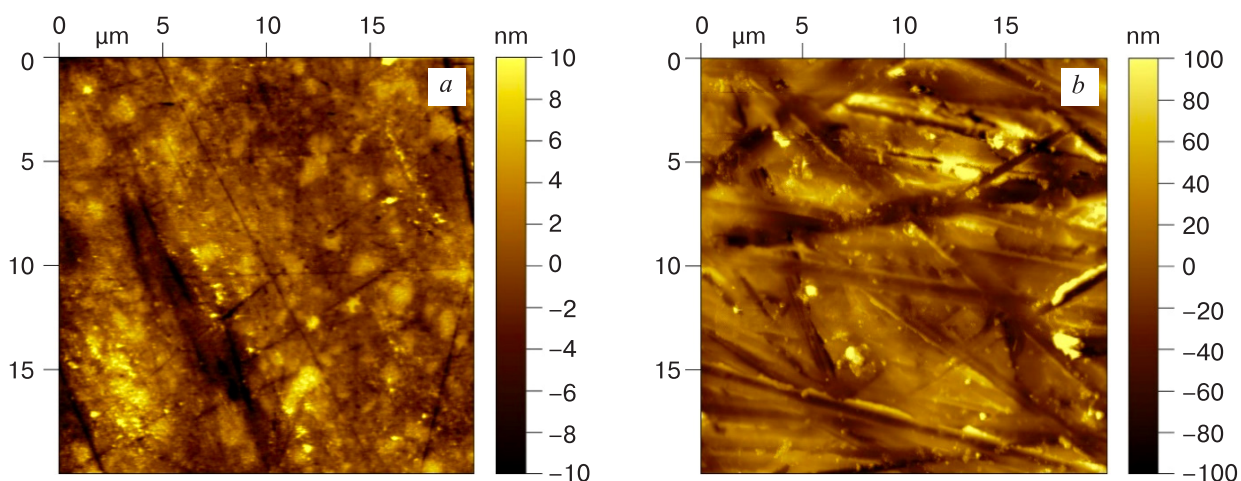


Figure 3. AFM images of the topography of the functionalized surface with PNIPAM film (a) and the initial FeRh substrate surface (b)

Atomic force microscopy (AFM) measurements have shown that the PNIPAM polymer has been successfully deposited on the FeRh substrate (Fig. 3). The AFM scans of the surface functionalized (Fig. 3a) and the initial sides of the FeRh substrate confirm the presence of the polymer layer.

Since the transition of PNIPAM with LCST has been observed in aqueous solutions, surface topography studies using AFM microscopy have been performed on the substrate soaked in distilled water at fixed temperatures above and below the LCST temperature. The AFM studies were performed on the substrate wetted with distilled

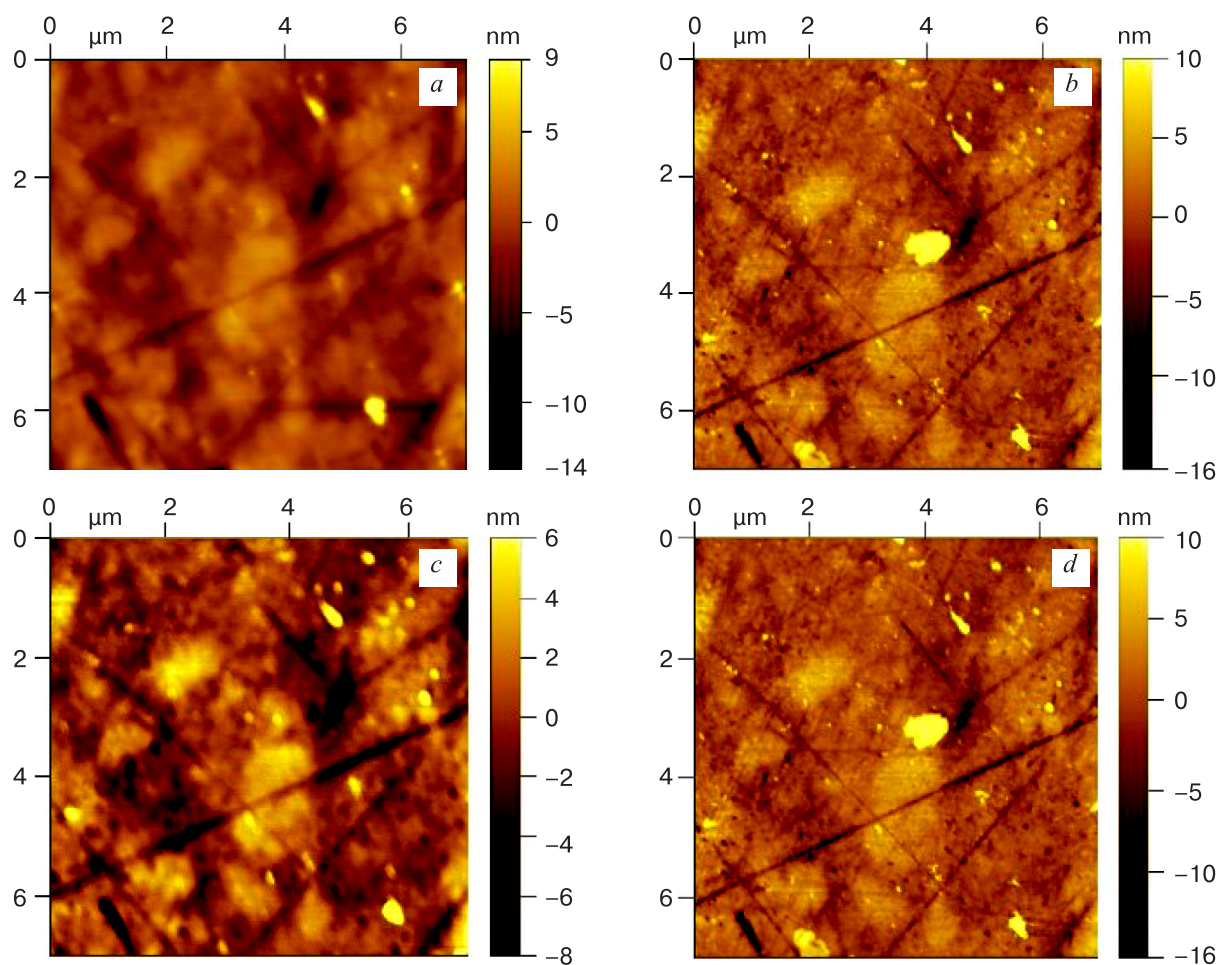


Figure 4. AFM images of the topology of the functionalized surface at different temperatures: (a) 30 °C, (b) 50 °C, (c) 40 °C, (d) 30 °C

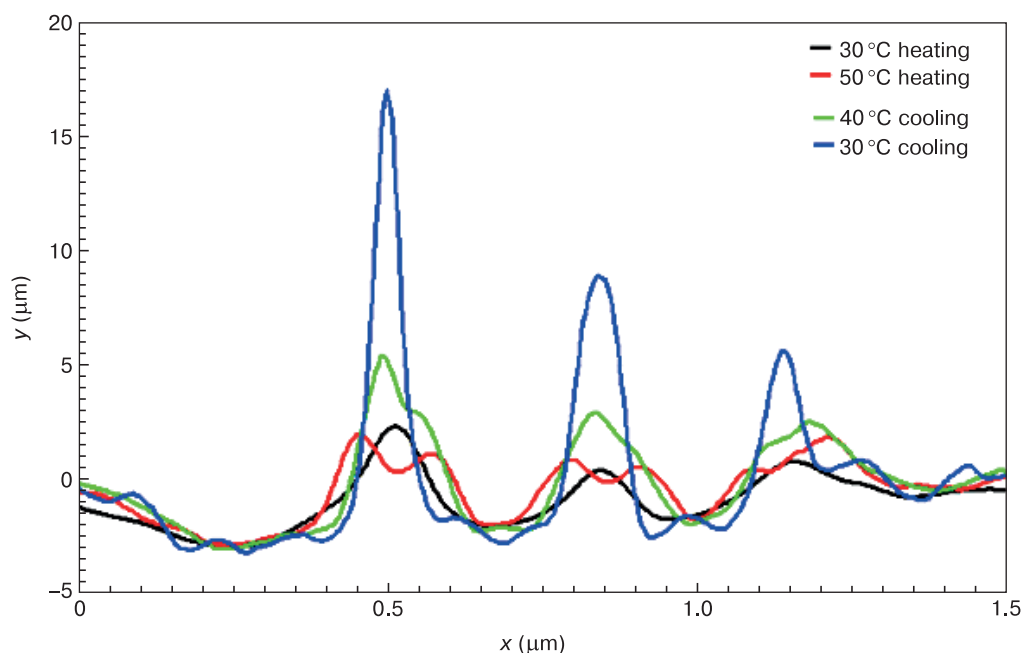


Figure 5. Surface profile in the selected area of the sample at temperatures of 30 °C, 50 °C, 40 °C and 30 °C

water at fixed temperatures both above and below the LCST temperature. The AFM analysis of the wetted PNIPAM surface at different temperatures ranging from 30 to 50 °C show some changes in the surface topology. Figure 4 shows AFM scans of the PNIPAM-coated $\text{Fe}_{49}\text{Rh}_{51}$ at different temperatures, starting at 30 °C, then heating up to 50 °C, followed by a cooling back to 30 °C.

Analysis of the surface profile in the selected area shown in Figure 5 revealed significant changes in structure after heating and cooling. When the temperature was raised to 50 °C, we observed a separation of the structural “hillock” into two separate peaks, which may be due to the dehydration of the polymer during the phase transition. This suggests the presence of areas from which liquid has been displaced during heating. Upon cooling back to room temperature, these peaks re-merge, indicating the re-absorption of liquid by the polymer. The profile scans in the selected areas at the selected temperatures were obtained in the area highlighted in red (Fig. 4b).

This behavior indicates that PNIPAM chemically polymerized on the surface of FeRh substrate and pre-wetted in water under heating experiences a transition with LCST and changes from hydrated gel-like state to wrinkled dehydrated state, displacing water that was absorbed by it in hydrated state. This change is reversible and occurs with a slight hysteresis, i.e., it does not completely return to the initial state, which is characteristic of this polymer. Similar behavior on films of crosslinked copolymer-isopropylacrylamide with polylactide (P(NIPAM-gPLA)), in which the change in Young's modulus and roughness from AFM measurements as a result of the transition from LCST was observed in [24]. To estimate the film thickness, we used an AFM probe to scratch the surface of the film. As the pressure applied to the probe increased, the

depth of the scratch remained below 5 nm. This indicates that the film's thickness is within this range. It should be note, that the technique used does not allow for accurate assessment of the film thickness. For more accurate measurements, in addition to AFM experiments, ellipsometry should be used, as was done for the PNIPAM series of films obtained under various technological condition [23]. As was shown, the collapse and corresponding changes in interfacial properties of PNIPAM depend on the grafting density and molecular weight, which were tuned by varying of polymerization time. The thickness of PNIPAM was depends on polymerization time and was varied in region: 4.6–59.9 nm (from AFM measurements) and 7.9–87.3 nm (from ellipsometry). Also, the changes of contact angle in LCST region depended on PNIPAM thicknesses (9.6–87.3 nm) were observed [23].

4. Conclusions

As the experimental results demonstrate, the proposed technological approach based on chemical polymer grafting can be used for fabrication of a thermosensitive polymer layer on the surface of FeRh magnetocaloric materials to implement the surface controlling concept at physiological temperatures using magnetic fields for potential biomedical applications.

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