

Preparation of Composite Hydrogels with Silica Nanoparticles by Photoinitiated Polymerization Reaction

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Geliş Tarihi: 25.07.2022

Kabul Tarihi: 25.02.2023

Abstract

In this study, (3-mercaptopropyl) trimethoxysilane (MPTMS) modified silica nanoparticles (SiO₂-MPTMS) were successfully prepared. The average size of SiO₂-MPTMS nanoparticles was measured by Dynamic Light Scattering (DLS) as 341 nm in ethanol, while Scanning Transmission Electron Microscopy (STEM) analyzes confirmed that the nanoparticles were nano-sized and revealed that their shapes were spherical. Then, 3D nanocomposite hydrogels were prepared by incorporating SiO₂-MPTMS nanoparticles in various ratios (0.25, 0.50, 0.75 and 1.0 wt %) into an acrylate resin consisting of *N*-isopropyl acrylamide (NIPAM) and polyethylene glycol diacrylate (PEGDA; as a crosslinker) by the photoinitiated polymerization reaction with Dimethoxy-2-phenylacetophenone (DMPA; as a photoinitiator). By Thermal Gravimetric Analyzer (TGA) measurements, it was determined that the nanocomposite hydrogels maintained their thermal stability up to 330 °C and the thermal degradation steps were close to each other. Scanning Electron Microscopy (SEM) study showed that the neat and nanocomposite hydrogels' morphological structures were in the porous and smooth scaffold, and also that the SiO₂-MPTMS nanoparticles (0.50 wt %) were homogeneously distributed in the network structures of hydrogels, localized in the bonds.

Keywords

Composite hydrogels;
Silica nanoparticles; 3-
Mercaptopropyl
trimethoxysilane; *N*-
isopropyl acrylamide;
Polyethylene glycol
diacrylate

Silika Nanopartiküller ile Kompozit Hidrojellerin Fotobaşlatılmış Polimerizasyon Reaksiyonu ile Hazırlanması

Öz

Bu çalışmada, (3-merkaptopropil) trimetoksilan (MPTMS) ile modifiye edilmiş silika nanopartiküller, (SiO₂-MPTMS) başarı ile hazırlandı. Dinamik Işık Saçılımı (DLS) ile SiO₂-MPTMS nanopartiküllerin ortalama boyutu 341 nm olarak (etanolde) ölçülürken, Taramalı Geçirimli Elektron Mikroskobu (STEM) analizleri nanopartiküllerin nano boyutlu olduğunu doğruluyarak partikül şekillerinin küresel yapıda olduğunu gösterdi. Daha sonra, ağırlıkça çeşitli oranlarda (% 0,25, % 0,50, % 0,75 ve % 1,0) SiO₂-MPTMS nanopartikülleri içeren *N*-izopropil akrilamid (NIPAM) ve polietilen glikol diakrilat (PEGDA; çapraz bağlayıcı) reçinelerinden oluşan formülasyonlar, Dimetoksi-2-fenilasetofenon (DMPA; fotobaşlatıcı) varlığında fotobaşlatılmış polimerizasyon reaksiyonuna uğratarak 3D yapıları nanokompozit hidrojeller hazırlandı. Termal Gravimetrik Analizör (TGA) ile, nanokompozit hidrojellerin termal kararlılıklarının 330 °C'ye kadar devam ettiği ve termal bozulma adımlarının, birbirleri ile yakın sıcaklık değerlerinde olduğu tespit edildi. Taramalı Elektron Mikroskobu (SEM) analizi ile saf ve nanokompozit hidrojellerin morfolojik yapıları incelendi ve bu malzemelerin, gözenekli ve pürüzsüz yapı iskeletine sahip oldukları ortaya koyuldu. Ayrıca, SiO₂-MPTMS nanopartiküllerinin (%0,50) ağ yapısı içerisinde, bağlarda lokalize olarak, homojen bir şekilde dağıldığı görüldü.

Anahtar Kelimeler

Kompozit hidrojeller;
Silika nanopartiküller;
3-Merkaptopropil
trimetoksilan; *N*-
isopropil akrilamid;
Polietilen glikol
diakrilat

1. Introduction

The preparation of composite hydrogels with inorganic nanoparticles is a remarkable issue as it provides improved behavior in morphological, thermal, and mechanical properties compared to traditional hydrogels (Zhao *et al.* 2020, Zhang *et al.* 2018, Aydinoglu *et al.* 2021). Application areas of composite hydrogels include materials such as adhesives, coatings, biomaterials, and microelectronics (Nguyen and West 2002, Neumann *et al.* 2007). In life science applications, silica nanoparticles are one of the most promising structures being used as fillers in the process of preparing composite materials (Lieberman *et al.* 2014, Sowan *et al.* 2018, Zou and Schlaad 2015). Silica nanoparticles, which are in polyorgano silane structures, are also important in material science due to their hybrid nature allowing the easy synthesis, low cost, and versatile modification of the surface of particles (Nakamura and Ishimura 2008, Balamurugan *et al.* 2010). The fact that they are easy to synthesize, provide an alternative range of particle sizes, excellent biocompatibility and hydrophilicity (Zou *et al.* 2008, Işin *et al.* 2009). On the other side, it is known that the surface modification of silica nanoparticles with various compounds such as polymers and biomaterials is more stable compared to gold nanoparticles (Vejayakumaran *et al.* 2008).

In nanoparticle studies, the particles are dispersed and housed in a suitable host material, such as a solvent, to protect them against external factors such as pH and temperature changes. But, it is possible to occur electronic and/or magnetic interactions between the solvent and the nanoparticle, which cause an irreversible aggregation of nanoparticles. The best way to avoid this problem is to covalently bonding on the surface of nanoparticles (Kickelbick *et al.* 2008, Bissadi and Weberskirch 2016). For this reason, the surface modification of silica nanoparticles is an important consideration. In this way, various functionalities are created on particle surfaces by substituting silanol groups of silica nanoparticles with some active chemical compounds (Nakamura and Ishimura 2008). These compounds with the selected

functional groups also allow grafting to the silica nanoparticle surfaces in addition to reducing filler agglomeration. Silane coupling agents involving alkoxy silane precursors have been widely used to modify the silica nanoparticle surfaces. These compounds, which perform a condensation reaction with silanol groups on the silica surface through alkoxy silane, also contain functional substituents such as vinyl, epoxide, amine and thiol (Oktay and Çakmakçı 2017, Liu *et al.* 2005). Among them, 3-mercaptopropyl trimethoxy silane with thiol functional group is an attractive molecule due to the ability of undergoing thiol-ene reaction (Irmukhametova *et al.* 2011, Kurttner *et al.* 2013). For the last decades, thiol-ene click chemistry has been an important reaction way for polymer chemistry due to enabling the modification of structures in versatile types. In this route, the photoinitiated thiol-ene reaction, which also offers some advantages such as shorter reaction times, minimizing the negative effects of oxygen, and accessing new molecular structures, has been studied in a wide range of applications such as coatings, biomaterials, and electro-optics, as a practical and efficient reaction method (Hoyle and Bowman 2010, Xi *et al.* 2014, Lowe 2010). However, the use of photoinitiated thiol-ene reaction to modify silica nanoparticles is an issue that still needs to be investigated in detail today. For these reasons, 3-mercaptopropyl trimethoxy silane (MPTMS), which is able to undergo thiol-ene reaction due to its thiol group, has to be investigated in detail as a silane agent, which uses in modifying silica nanoparticles being involved in the preparation of various composite materials in a wide field. Although there are various studies investigating the thiol-ene click reaction for the use of surface-modified silica nanoparticles in 3D composite systems, the number of studies in which 3-mercaptopropyl trimethoxy silane agent is modified on silica nanoparticles and applied in various polymer matrices is very limited (Irmukhametova *et al.* 2011, Kurttner *et al.* 2013). In literature, Wu *et al.* prepared UV-cured coatings with di- and tri-functional acrylate systems (epoxy and tripropylene glycol diacrylates, and trimethylolpropane triacrylate) in presence of the silica nanoparticles

whose surfaces were modified with MPTMS (Wu *et al.* 2013). As a part of the author's interest in silica nanoparticles, it was studied with a MPTMS modified nanoparticles as fillers in a thiol-ene resin system including a difunctional epoxy dimethacrylate and a 3-arm thiol acrylate (bisphenol A glycerolate dimethacrylate and trimethylolpropane tris(3-mercapto propionate, respectively) as a first in the literature (Karaca 2021). However, in the literature, it has not been studied to the preparation of a nanocomposite hydrogel with *N*-isopropyl acrylamide (NIPAM) and polyethylene glycol (PEG) containing silica nanoparticle fillers modified with MPTMS. For this reason, in this study, nanocomposite hydrogels were prepared by photoinitiated polymerization with NIPAM and PEG diacrylate in the presence of MPTMS-modified silica nanoparticles. Then, the physical, thermal, and morphological properties of these composite hydrogels were investigated.

2. Materials and Methods

2.1. Materials

Tetraethyl orthosilicate 98% (TEOS), (3-mercaptopropyl) trimethoxysilane 95% (MPTMS), *N*-Isopropyl acylamide (NIPAM), polyethylene glychol diacrylate (PEGDA; Mn= 700) and 2,2-Dimethoxy-2-phenylacetophenone 99% (DMPA, as a photoinitiator) were all purchased from Sigma-Aldrich. Ammonia solution (25%) and all solvents were purchased from Merck. All of the chemical reagents were used as received.

2.2. Preparation of silica nanoparticles

The silica nanoparticles were synthesized according to the Stöber method (Stöber *et al.* 1968). 68 mg (1 mmol) of ammonia (25-30%) and 1.98 g (110 mmol) of deionized water were mixed in 100 mL of methanol in a 250 mL single neck round bottom flask, and the reaction mixture was stirred for 20 minutes. Then, 10.41 g (50 mmol) of TEOS was added dropwise to the mixture and the solution was stirred for 3 days. The resulting reaction solution was precipitated in 150 mL of hexane and diethyl ether solution (2:1), then the precipitated particles were dried in vacuo.

2.3. Surface modification of SiO₂ nanoparticles

2.5 g silica particles dispersed into 300 ml dry toluene in a 250 ml one necked flask on ultrasonic bath. The reaction flask was equipped with a dropping funnel and condenser on a magnetic stirrer. 5 g silane compound agent MPTMS was added dropwise for an half hour at room temperature. After the reaction mixture was stirred on 600 rpm for overnight at 80 °C, the particles were isolated via centrifugation at 10000 rpm for 15 min and washed several times with ethanol to remove the non-bonded MPTMS. Lastly, the synthesized SiO₂-MPTMS nanoparticles were dried in vacuum.

2.4. Preparation of nanocomposite hydrogels

The hydrogels were synthesized by photoinitiated polymerization reaction. At first, SiO₂-MPTMS nanoparticles (0.25, 0.50, 0.75 and 1.0 % by weight of the formulation (wt %)) were dispersed in deionized water (10 ml) by ultrasonication for 10 min. Then, a solution containing 20% by weight of a mixture of NIPAm and PEGDA (Mn: 700) in desired weight ratios (1:0.25) for each was prepared in SiO₂-MPTMS nanoparticles dispersed deionized (DI) water. Also, DMPA (0.1 wt %) was added to the prepared solutions. Subsequently, the photoinitiated polymerization reaction was carried out by irradiating the formulations for 60 minutes in an air-cooled photoreactor consisting of 8 UV lamps with a maximum wavelength emission of 365 nm. The nomenclature used for the various hydrogels discussed in this study is given in Table 1.

2.5. Instrumentation and methods

FT-IR analysis was performed to characterize the chemical structures of the products on a Perkin-Elmer 100 FT-IR spectrometer with an attenuated total reflectance (ATR) cell equipped with a ZnSe single crystal, in the frequency range of 4000–650 cm⁻¹ at a resolution of 4 cm⁻¹.

A dynamic Light Scattering (DLS) study was performed with a dilute solution of nanoparticles prepared by dispersing in a solvent (ethanol) medium (approximately 0.1 mg/mL) to measure

their average size distribution at 25 °C using Nano-S Zetasizer (Malvern Instruments).

Scanning and Scanning Transmission Electron Microscopy analyzes (SEM and STEM, respectively) were performed by a Philips-FEI XL30 ESEM-FEG SEM. For STEM measurements, dilute dispersions of nanoparticles were prepared in a solvent (ethanol; 0.1 mg/1 mL), and then particle sizes were observed at 300,000x and 350,000x magnification. In SEM analyzes, it was studied with freeze-dried hydrogels. Samples were prepared by freezing in liquid nitrogen followed by slicing quickly and then they were covered by gold (Au). After that, cross-section images of these samples were measured at 2,000x, 5,000x, and 10,000x magnification.

A Perkin ELMER TGA 8000 analyzer was used to perform thermal gravimetric analyzes (TGA) of nanocomposite hydrogels under a nitrogen atmosphere (50 mL/min) using an alumina sample pan with a heating rate of 10 °C/ min from room temperature to 610 °C.

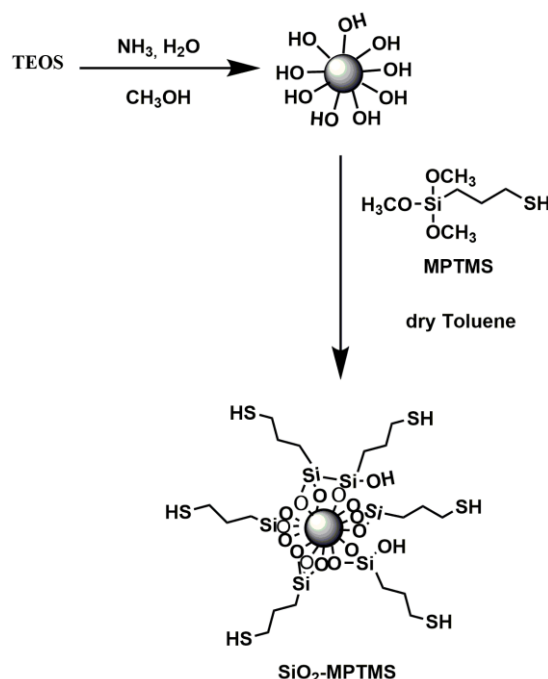
The swelling characteristics of the hydrogels were investigated for at least three samples which were a mass of 0.300 ± 0.1 g, were placed into a beaker filled with deionize water at room temperature. The wet weight of the hydrogels were measured and then, compared with their dry masses in order to calculate the percent swelling content (%) with the formula in Eq. (1):

$$\text{Swelling (\%)} = (W_s - W_d) / W_d \times 100 \quad (1)$$

W_d and W_s are the weight of the dry and swollen hydrogels, respectively.

3. Results and Discussion

Silica nanoparticles which were modified with MPTMS as shown in scheme 1, were characterized by FT-IR spectroscopy. Then, the average size distribution of MPTMS modified silica nanoparticles was measured by DLS. Also, the morphologies of SiO_2 -MPTMS nanoparticles were investigated by STEM in addition to observing their sizes.



Scheme 1. Preparation of SiO_2 -MPTMS nanoparticles.

FT-IR spectroscopy is recognized as a powerful tool to characterize the chemical structure of surface-modified nanoparticles (Zou *et al.* 2008). Figure 1 shows the FT-IR spectrum of MPTMS modified nanoparticles. It was observed that the stretching of aliphatic groups at 2964 cm^{-1} and 2853 cm^{-1} due to the propyl group of MPTMS silane agent, in addition to the strong absorption of Si-O-Si groups of silane group and silica core at 1054 cm^{-1} .

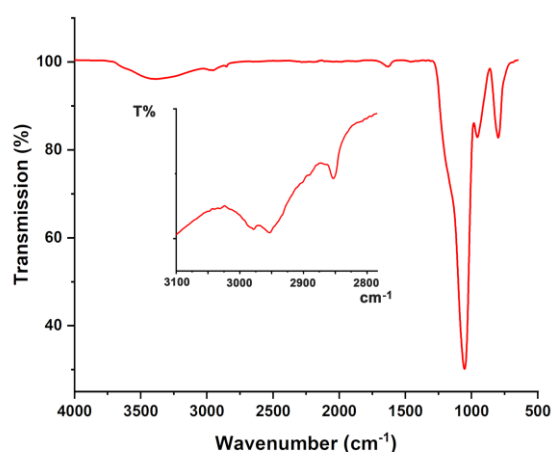


Figure 1. FT-IR spectrum of SiO_2 -MPTMS nanoparticles.

The size of MPTMS modified nanoparticles was measured by DLS as 341 nm (Pdl: 0.543) in average

(as shown in Figure 2). Figure 3 shows the STEM images of SiO₂-MPTMS nanoparticles. STEM study indicated that the nanoparticles being have spherical shapes, in nanometer size. The size of nanoparticles is assumed as an attractive benefit in advanced nanocomposite materials (Ashraf *et al.* 2018).

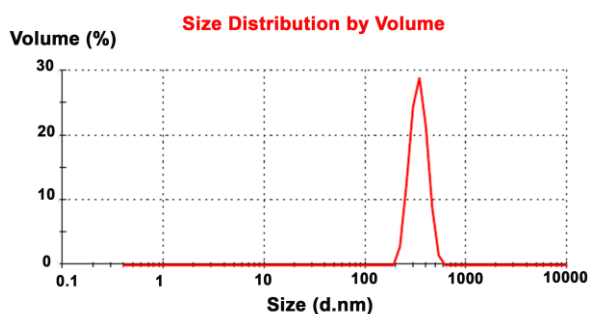


Figure 2. DLS spectrum of SiO₂-MPTMS nanoparticles in ethanol (0.1 mg/ mL).

Photoinitiated polymerization of NIPAM with a PEGDA crosslinker was achieved for various formulations which consisted of SiO₂-MPTMS nanoparticles in the presence of DMPA as a photoinitiator. The gravimetrically determined ratios of components presenting in the formulations were listed in table 1 as shown their nomenclatures.

The chemical structure of SiO₂-MPTMS added nanocomposite hydrogels containing 0.5% and 1.0% wt contents were confirmed by FT-IR spectra in comparison with the neat hydrogel (as shown in Figure 4). All of the FT-IR spectra of hydrogels exhibit broad bands of N-H stretching at around 3280 cm⁻¹ and 1538 cm⁻¹, and the strong peak of carbonyl stretching at around 1640 cm⁻¹, while the vibrations of Si-O-Si and Si-O bonds were clearly observed at around 1095 cm⁻¹ in the curves of Hydrogel0.5Np and Hydrogel 1Np since they contain SiO₂-MPTMS nanoparticles.

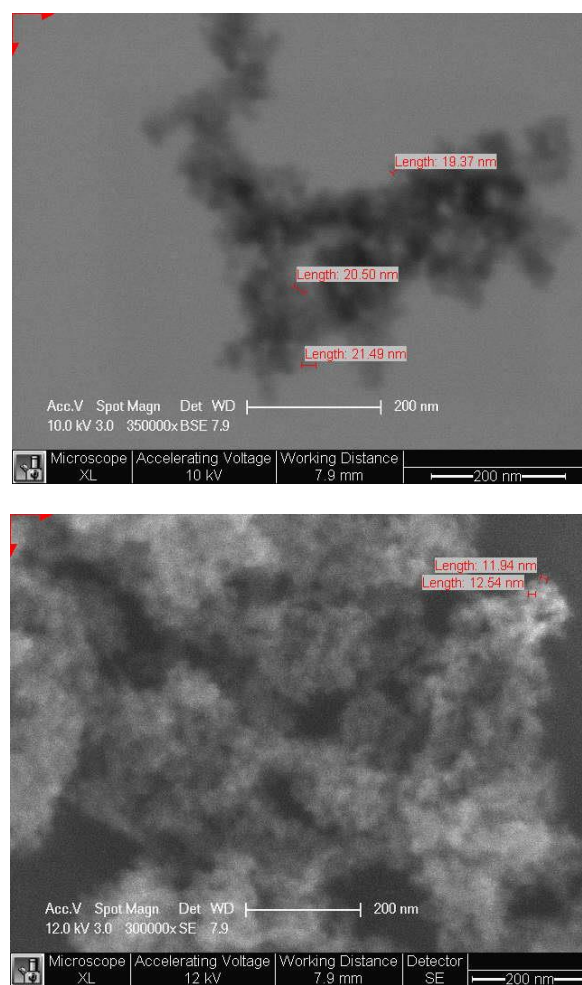


Figure 3. STEM images of SiO₂-MPTMS nanoparticles.

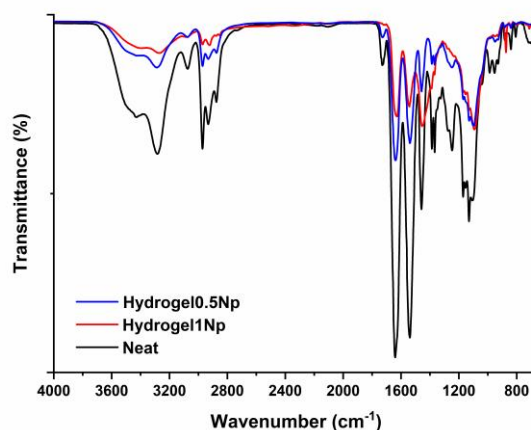


Figure 4. FT-IR spectra of nanocomposite hydrogels (Hydrogel0.5Np and Hydrogel1Np) with a comparison of Neat Hydrogel.

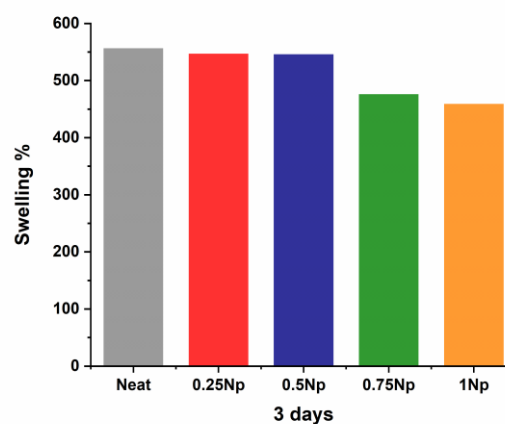
Table 1. List of formulations of nanocomposite hydrogels.

Formulations	NIPAM (wt %)	PEGDA	SiO ₂ -MPTMS Nanoparticles (wt %)	PI (wt %)
Neat	20	+	-	+
Hydrogel0.25Np	20	+	0.25	+
Hydrogel0.50Np	20	+	0.50	+
Hydrogel0.75Np	20	+	0.75	+
Hydrogel1Np	20	+	1.0	+

PEGDA: polietilen glikol diakrilat (Mn: 700), its weight ratio is 0.25 according to NIPAM (0.25: 1); PI: Photoinitiator (DMPA), 0.1 percent by weight of the resin.

Changes in gravimetry of hydrogels kept in deionized water were determined by swelling tests performed by measuring according to their initial (dry) weight. When the swelling capacity of the gels was examined against time, it was observed that the absorbed water and the stability of the network were equilibrium at the end of the 3rd day (72 h). Figure 5 shows the percent swelling values of hydrogels measured as 547.1%, 546.24%, 476.14% and 459.13% in 0.25%, 0.50%, 0.75% and 1.0% particle content and 556.52% for neat hydrogel for 3 days. The percent swelling ratios of the hydrogels strongly depended on the content of SiO₂-MPTMS nanoparticles. A decrease in the swelling ratios appeared with the increasing SiO₂-MPTMS content (from 0.25% to 1.0%) due to an increase in the hydrophobic group number. On the other side, It is known that fast polymerization rates cause less swelling (Karaca *et al.* 2010). Higher nanoparticle content with thiol groups resulted in more extensive cross-linking of the polymer network, which determined the diffusion of water in the network.

The thermal and morphological properties of nanocomposite hydrogels were investigated according to the amount of nanoparticles, between 0.25 and 1.0 wt % in polymer matrice.

**Figure 5.** Percent swelling capacity results of nanocomposite hydrogels for 3 days.

TGA study was performed to investigate the thermogravimetric behavior of nanocomposite hydrogels according to the amount of SiO₂-MPTMS nanoparticles in polymer matrice and/ or covalently attached polymer network owing to thiol groups (as shown in Figure 6). The TGA thermograms showed the thermal degradation of the polymer network between 330 °C and 450 °C as a characteristic weight loss, in addition to the thermal decomposition up to 100 °C due to the moisture content.

The 5%, 10%, and 50% decomposition temperatures (named Td5, Td10, and Td50, respectively) are given in Table 2. As can be seen from the TGA data, the td10 and the mid-point (td50) degradation temperatures were higher for the nanocomposite hydrogels named Hydrogel0.25Np, Hydrogel0.5Np and Hydrogel1Np according to the neat one. In contrast, Td5 temperature values showed the presence of moisture, especially in Hydrogel0.75Np. Higher thermal stability in nanocomposite hydrogels attributed to chemical interactions between SiO₂-MPTMS nanoparticles and NIPAM resulted from the possibility that the thiol groups surface on the nanoparticles can undergo thiol ene reaction with the vinyl bond of NIPAM. Additional linkages in the network due to the nanoparticle contents might lead to the restricted molecular mobility of the polymer chains, which inhibits the diffusion of the decomposed product in the polymer matrix (Işın *et al.* 2009).

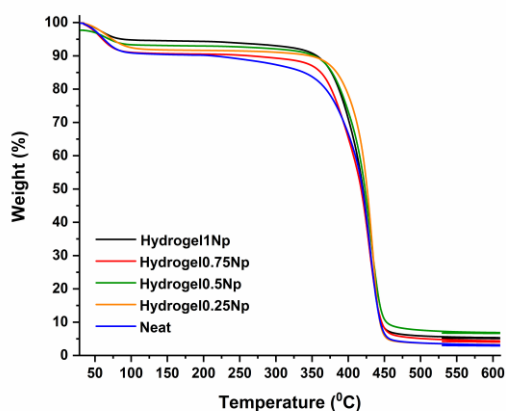


Figure 6. TGA thermograms of nanocomposite hydrogels containing SiO₂-MPTMS nanoparticles and the comparison with the neat hydrogel.

Table 2. Thermal properties of carbazole based vinyl functional polysiloxane copolymers

Samples	Td5 ^a (°C)	Td10 ^a (°C)	Td50 ^a (°C)
Neat	62	213	418
Hydrogel0.25Np	74	346	426
Hydrogel0.5Np	69	353	423
Hydrogel0.75Np	60	264	418
Hydrogel1Np	88	356	420

^aCalculated from weight loss versus temperature curve of TGA thermogram.

^bThe percent char (Yc) content of the solid residue was analyzed by TGA at 600 °C in a nitrogen atmosphere.

The morphological properties of the hydrogel with SiO₂-MPTMS nanoparticles (0.5 wt %) were investigated comparing with neat hydrogel. Figure 7 shows the SEM images of neat and hydrogel0.5Np hydrogels. The pore structures of hydrogels could greatly influence their properties, such as mechanical properties and drug release kinetics, by enabling the preservation of the hydrated state of the hydrogel (Newhama *et al.* 2022). SEM images revealed porous and smooth scaffold structures with variable forms and pore sizes for both neat and Hydrogel0.5Np. The hydrogel containing SiO₂-MPTMS nanoparticles had a homogeneous network structure, but it was observed that the addition of nanoparticles leads to a decrease in the pore size of the microstructures compared to the neat substance. In addition, it was observed that SiO₂-MPTMS nanoparticles were homogeneously dispersed in the polymer matrix, where they were attached to the bonds forming the network structure, not to the pores of the material. This result showed that these nanoparticles were included in the network structure by chemical links through thiol groups.

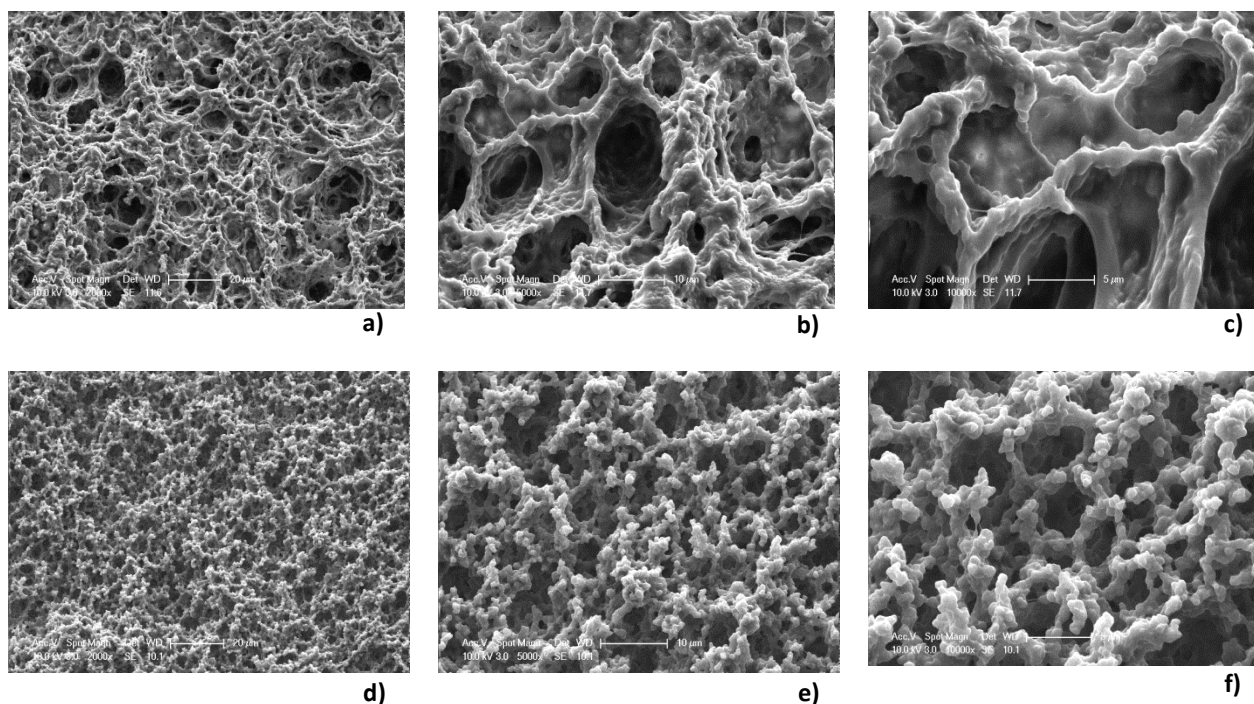


Figure 7. SEM images of neat hydrogel (a, b, and c), and nanocomposite hydrogel: Hydrogel0.5Np containing SiO₂-MPTMS nanoparticles in a ratio of 0.50 wt % (d, e, and f). The scale bars are 20 μm, 10 μm and 5 μm, respectively.

4. Conclusion

The SiO₂-MPTMS nanoparticles were successfully prepared. While the FT-IR spectrum of SiO₂-MPTMS nanoparticles confirmed the surface modification by the stretching of propyl group vibrations of MPTMS silane agent, the average size of these modified nanoparticles was measured as 341 nm in ethanol by DLS. In addition, STEM study showed that nano-sized nanoparticles were spherical shapes.

SiO₂-MPTMS nanoparticles involving hydrogels were prepared by photoinitiated polymerization reaction performed along with NIPAM in the presence of PEGDA as a crosslinker with DMPA as a photoinitiator in various formulations consisting of 0.25 to 1.0 % by weight (wt %) particle content. The swelling ratios of hydrogels were measured as 556.52%, 547.1%, 546.24%, 476.14% and 459.13% for neat and SiO₂-MPTMS involving hydrogels (0.25%, 0.50%, 0.75% and 1.0%, respectively) for 3 day. TGA study revealed that neat and composite hydrogels were in close decomposition temperatures. SEM images showed that both neat and composite hydrogels had porous structures,

and also SiO₂-MPTMS nanoparticles were homogeneously dispersed in the polymer network.

Acknowledgment

Yalova University and Yalova University Scientific Research Projects Coordination Unit are acknowledged for the financial support (Project No: 2019/AP/0005).

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