Mechanics of Advanced Composite Structures 4 (2017) 1-8

Semnan University

Mechanics of Advanced Composite Structures

journal homepage: http://MACS.journals.semnan.ac.ir

Synthesis and Characterization of Polymer/Nanosilicagel Nanocomposites

F. Shakooee, M. Yousefpour*, M. Tajally

Faculty of Materials and Metallurgical Engineering, Semnan University, Semnan, Iran

PAPER INFO

Paper history:
Received 2016-06-28
Revised 2016-11-08
Accepted 2016-12-04

Keywords:
Nanocomposite
Biocompatible polymer
Silica
Sol-gel
Refractive index
Rheology
Intraocular lenses

ABSTRACT

In this study, a polymer-silica nanocomposite using the sol-gel method was synthesized in three steps at room temperature. The nanocomposite material was formed with an organic compound (polyethylene glycol) and inorganic silica nanoparticles. Furthermore, the size and the distribution of nanoparticles in the polymer matrix were characterized by a transmission electron microscope (TEM). In addition, the refractometer analysis was used to measure the refractive index of the nanocomposite. Following that, Fourier transform infrared (FTIR) spectroscopy and small-angle X-ray diffraction and high X-ray diffraction have also used to characterize the polymer and the inorganic part of the nanocomposite. TEM studies showed the distribution of nanoscale silica particles of the size of 50-100 (nm) in the polymer matrix. Furthermore, the refractive index of the nanocomposite was measured about 1.4, which was very close to the refractive index of the natural lens (1.411). Additionally, the FTIR spectra showed OH groups in FTIR spectroscopy, which confirmed the hydrophilic property of silica nanoparticles and the two sharp peaks at the angles of 19° and 23° in the X-ray diffraction analyses, which were in the nature of the crystallinity of polyethylene glycol. Finally, the results showed the surface modification of nanoparticles and their incorporation in a polymer matrix, which led to the formation of the desired nanocomposite that was made of inorganic (silica nanoparticles) and an organic (polyethylene glycol) compound.

DOI: 0.22075/MACS.2016.500

1. Introduction

The use of biopolymers in combination with silica nanoparticles has been studied in biotechnology. For example, biopolymer-silica nanocomposites are considered for advanced medical materials, such as tissue engineering, encapsulation and production of bio-sensors and bio-reactors [1]. Nanocomposites have unique properties for academic research and the development of innovative industrial materials. Nanocomposites have the unique properties of organic and inorganic materials. Therefore, inorganic nanoparticles must be distributed uniformly to develop composites' properties in the polymer matrix. Furthermore, the surface of nanoparticles must be modified with absorbed or grafted to polymers with small molecules, such as silane coupling agents, to improve the dispersion, stability and compatibility of nanoparticles with solvents or polymeric materials. Surface modification can improved the surface reactions between nanoparticles and the polymer matrix, which leads to obtaining unique properties, such as high toughness, as well as optical and electronic properties. Thus, the surface modification of inorganic nanoparticles is needed to produce organic-inorganic nanocomposites with high performance [2]. The different types of macromolecules are combined to form gels with outstanding physical properties in nature. One of the natural organs is the lens, which projects the optical image on the retina together with the cornea. The lens is a biconvex spheroidal tissue. It is encapsulated within an elastic collagenous [3,4]. The ability to accommodate nearby targets gradually diminishes with increasing age and then glasses or bifocals are needed for reading. This phenomenon is known as the presbyopia [3].

* Corresponding author. Tel.: +98-23-33383385; Fax: +98-23-33654119

E-mail address: myousefpor@semnan.ac.ir

The presbyopia is a condition in which the eye loses its ability to accommodate or focus on nearby objects due to the hardening of the natural crystalline lens [5]. The idea of adaptation can be adjusted by replacing the opaque lens that mimics materials similar to those of the human crystalline lens [6-8]. These materials must be soft and transparent. Furthermore, they have a refractive index close to that of the natural lens [9-12]. Moreover, they must be biocompatible, maintain their stability over time and be capable of being trapped in a capsular bag easily [13-15]. The studies related to accommodative intraocular lenses focus on several materials [16-19]. These studies address the properties of that materials that are related to intraocular lenses. However, the investigation of the atomic and molecular structure of nanostructured composite materials, which are used as injectable lenses, is limited. For example, the effect of nanoparticle size and distribution on the final properties of the nanocomposites, the degree of crystallinity of the polymer matrix, the surface modification of nanoparticles and matrix materials, hydrophilicity and hydrophobicity properties are important. In this study, the silica nanoparticles of the size of 50 to 100 nm were placed in the matrix of a polyethylene glycol polymer. Meanwhile, the refractive index of the nanocomposite depended on the nanoparticles. The elastic behavior of the nanocomposite is controlled by the polymer matrix. In addition, the use of the polymer will induce the possibility of a benefit of the nanocomposites in biological and medical applications. In this study, nanoparticles were modified with a silane coupling agent and polymer chains with an octadecan group. After the appropriate concentration of the organic and inorganic compounds was prepared, the samples were synthesized and then the properties were studied using X-ray diffraction, FTIR spectroscopy, refractometery and rheometery evaluation.

2. Experimental Section

2.1 Materials and methods

In this study, the nanostructured polymer-silica using the sol-gel method was prepared [3]. To synthesize it, 3-aminopropyltrimethoxysilyl (APTMS, 98%, Merck) was used as the silica source and silane coupling agent. Furthermore, methanol (CH_4O, 99.8%) and 1,4-dioxane ($C_4H_8O_2$,99%) were used as a solvent of APTMS and PEG, respectively. Besides, hydrochloric acid (HCl, Merck), 1-bromooctadecane ($C_{18}H_{37}Br$, 97%, Merck), poly (ethylene glycol) monomethoxy ether (PEG, M_n=5000) and sodium hydride (Sigma Aldrich) were used to synthesize samples. To deposit the organic compound, diethyl ether was purchased from M&B Company.

2.2. Preparation of the inorganic compound (OCAPS)

In the first step, 100 ml of the Bis [3-(trimethoxysilyl) propyl] amine was dissolved in 800 mL of methanol. Then, 135 ml of hydrochloric acid was added by stirring. The mixture obtained was stirred for a week until OCAPS (white powder) was precipitated. The OCAPS obtained was washed with methanol and then dried.

2.3. Preparation of the organic compoud

In this section, 5 g polyethylene glycol in 100 ml of 1,4-Dioxane was completely dissolved. Then, 0.18 g of sodium hydride was added. The mixture was stirred for one hour. Furthermore, 6.2 mL of 1-bromooctadecane was added drop by drop for an hour. The final solution was stirred for 24 hours at room temperature and then precipitated by adding 200 ml of diethyl ether.

2.4. Preparation of nanostructured composite material of polyethylene glycol - Silica (PEG/SiO_2)

The nanocomposite of organic-inorganic was prepared. The concentration of the organic compound was selected in an aqueous solution at a constant amount, because the main goal of this work is the development of a novel injectable accommodative lens for intraocular applications, which is related to a thermosensitive, hydrophobically modified poly (ethylene glycol) - silica nanoparticles. This nanocomposite has the advantage of being able to form a gel, which completely fills the capsular bag and improves the elastic modulus. Therefore, the concentration of the organic compound must be selected constant amount. Thus, in this study, the concentration of the organic compound was kept constant at 30% wt and the inorganic concentration varied from 0 to 45% wt. A different concentration of aqueous solution was prepared to detect the suitable concentration at the end of the experiments.

2.5. Characterization polyethylene glycol compound reinforced with silica nanoparticles

X-ray diffraction (BRUKER, D8-Advanced model) analysis was used to confirm the amorphous OCAPS powder. The voltage and current were 40Kv and 30mA, respectively. X-rays were produced by anode copper with Cu-Kα radiation with a wavelength of 1.54Å. The scan rate in the small-angle XRD analysis and high-angle analysis were considered to be about 0.01 degree/min and 0.065 degree/min, respectively. To confirm the surface modification of the organic and inorganic analysis of polyer-silica nanocomposte gel, FTIR spectroscopy (8400S model-making company Shinadzu) was used. To determine the size and distribution of the silica nanoparticles in the

matrix of polyer-silica, nanocomposte gel was used by the transmission electron microscope (Zeiss - EM10C - 80 KV Germany). Furthermore, before the refractive index test, the polyer-silica nanocomposte gel samples were vibrated with an ultrasonic machine (Misonix – S3000 model, 2,500 ml). To determine the refractive index of the polyer-silica nanocomposte gel, the refractometer analysis was used with the refractometer (ATAGO model, 1T, 1.3-1.7 range and accuracy of ±0.0002). To investigate the pass and absorption of the light in the polyer-silica nanocomposte gel, UV-Vis (UV-1800 model, Shimadzu company) was used. Viscoelastic properties of the nanocomposites were studied using a rheometer with a CC27 measuring system (MCR300 model, Anton-Paar Company). To shear a strain of 1%, a fixed frequency of 1 s^{-1} was applied to determine the storage modulus and loss modulus of polyer-silica nanocomposte gel.

3. Results and Discussion

Figure 1 shows a broad peak in the range of 15-35° that reveals the amorphous silica phase. Similar results were obtained in previous investigations [20,21]. The structural disorder of silica phase by X-ray diffraction with a small angle (below 10°) is also shown in Figure 2. Figure 3 shows the X-ray diffraction diagram of the treated polyethylene glycol. There are two sharp peaks at about 19° and 23°, which indicates the nature of the crystalline of PEG [22,23]. The crystalline PEG causes a good encapsulation, no chemical change during the implantation process and excellent thermal stability in the nanocomposite obtained. The percent crystallinity is obtained from the crystalline peak area divided by the total area under the graph of the intensity angle of the X-ray diffraction pattern and by using Equation 1, in which X_c is the degree of crystallinity, Aa is the amorphous surface and A_c is the crystalline surface. The amount of the A_a and A_c are calculated by Excel software.

$$X_c = 1-(A_a/(A_a+A_c)) \quad (1)$$

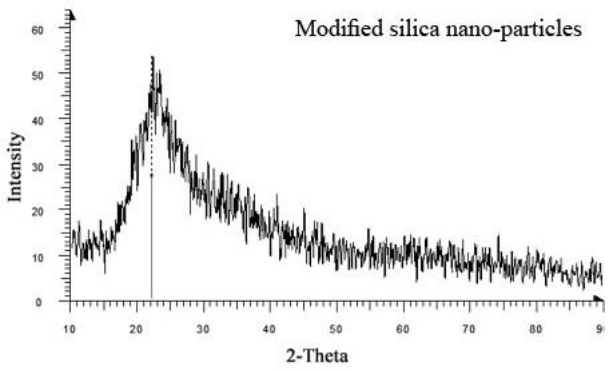

Figure 1. High-angle X-ray diffraction pattern of the silica nanoparticles modified with APTMS

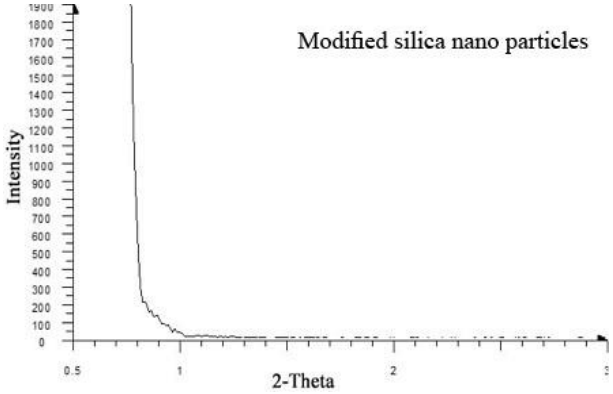

Figure 2. The small-angle X-ray diffraction pattern of the silica nanoparticles modified with APTMS

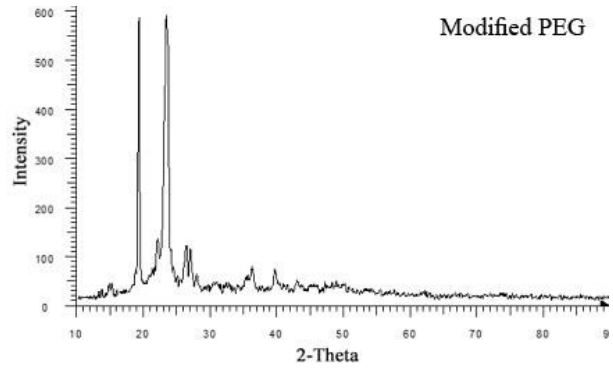

Figure 3. The high-angle X-ray diffraction pattern of polyethylene glycol modified with the Octadecan group

Several ways were studied to deal with the accumulation of the nanoparticles and their uniform distribution in the polymer substrate. One of the methods was surface modification of the nanoparticles using a coupling agent. This material has active functional groups. Thus it reacts with hydroxyl groups on the surface of nanoparticles, such as nanosilica particles and nanoparticles; therefore, sticking the hydroxyl groups to the surface of nanoparticles increases the hydrophobic property due to enhancing the contact angle. [24]. The schematic of the coupling of hydroxyl groups on the surface of nanocomposite is shown in Figure 4 [30]. Figure 5 shows the FTIR analysis of the nanoparticles modified with APTMS. Table 1 classifies the functional groups attributed to the absorptions obtained from these spectra. Furthermore, Figure 6 shows the Fourier transform infrared diagram of the treated polyethylene glycol.

Table 1. The functional groups of the modified silica nanoparticles appearing according to the FTIR analysis

Wavenumber (cm^{-1})	Assignment
459	Si-O
694	Si-O
794	Si-O
960	Si-OH
1086	Si-O-Si
1568	H-O-H, N-H
2924	C-O

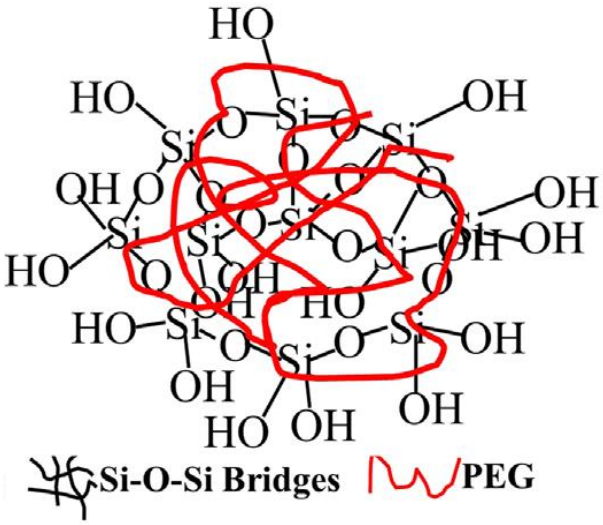

Figure 4. Schematic of the sticking of hydroxyl groups.

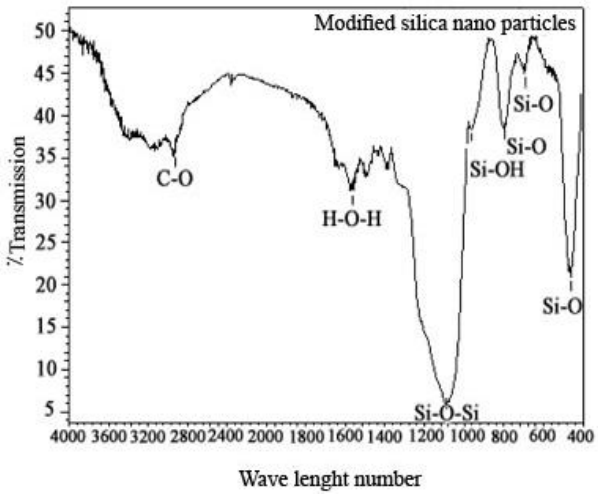

Figure 5. FTIR analysis of the silica nanoparticles modified with APTMS.

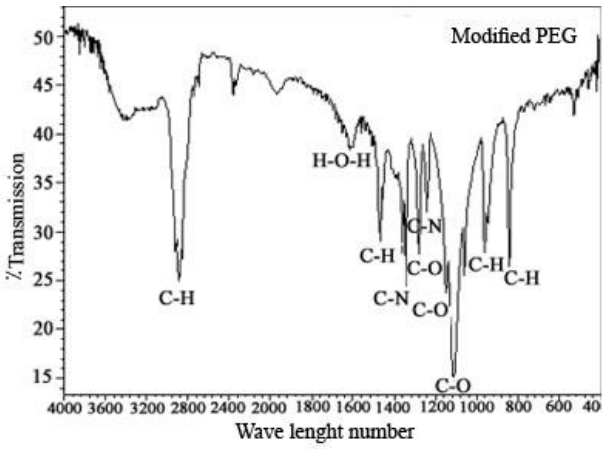

Figure 6. FTIR analysis of the processed and modified polyethylene glycol with the Octadecan group.

As shown in Figure 6, all peaks are related to the connecting link of the treated polyethylene glycol, which are briefly summarized in Table 2.

Table 2. The functional groups that appeared according to the FTIR analysis of the treated polyethylene glycol.

Wavenumber (cm^{-1})	Assignment
842	C-H
962	C-H
1,060	C-O
1,113	C-O
1,150	C-O
1,242	C-N
1,280	C-O
1,342	C-N
1,468	C-H
2,889	C-H

It should be noted that two bond peaks appeared in the 2,359 cm^{-1} and 2,694 cm^{-1} wavelengths. These peaks indicate the tension bond of silanols. The absorption bond of 3,417 cm^{-1} and 1,614 cm^{-1}, has appeared in the FTIR spectra of the nanocomposite. These absorption peaks have been attributed to the OH^- groups of moisture absorption from the environment [25]. These peaks are observed in the spectra of the composite, which confirms the hydrophilic nature of silica nanoparticles. And the absence of this peak in the spectrum of the polymer proves the hydrophobic nature of the polyethylene glycol. The groups of water molecules are usually observed at wavelengths 1,644cm^{-1}. However, in the prepared nanocomposites, the functional groups are formed with slightly lower wavelengths [23]. This is related to the loss of water molecules because the surface of silica nanoparticles is covered with APTMS. Generally, the peaks from 1,350cm^{-1} to 1,440 cm^{-1} indicate polymers with very small changes [26]. The functional groups attributed to the absorption peaks by an FTIR analysis of the nanostructured composite material of polyethylene glyco -silica were shown in Table 3 and Figure 7.

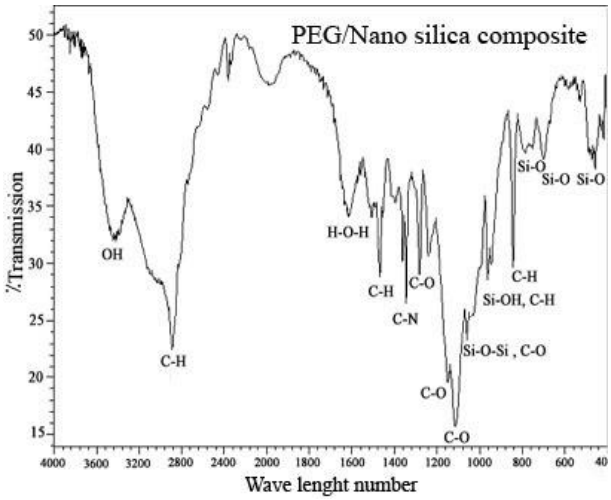

Figure 7. FTIR analysis of nanostructured composite material of polyethylene glycol-silica.

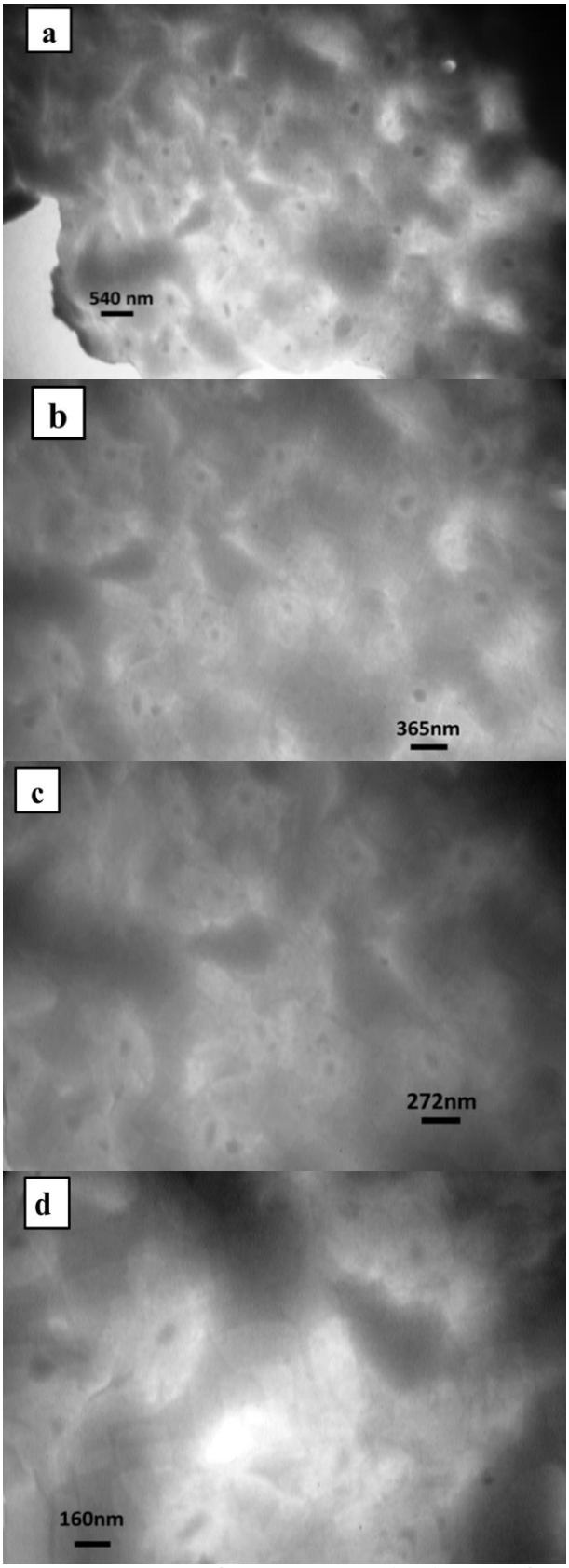

Figure 8. Transmission electron microscope (TEM) images taken from a nanostructured composite material of polyethylene glycol -silica. (a) magnified 4,000 times, (b) magnified 6,300 times, (c) magnified 8,000 times, (d) magnified 12,500 times.

Table 3. The functional groups that appeared according to the FTIR analysis of the nanostructured composite material polyethylene glycol-silica.

Wavenumber (cm^{-1})	Assignment
842	C-H
962	C-H , Si-OH
1,060	C-O , Si-O-Si
1,112	C-O
1,150	C-O
1,280	C-O
1,342	C-N
1,468	C-H
1,614	H-O-H, N-H
2,887	C-H
3,417	O-H [Fig. 4], N-H

Figure 8 displays the distribution of the nanoparticles of silica in the matrix of the polymer. The TEM images in various magnifications of silica nanoparticles show the size of the nanoparticles, which is from 50 nm to 100 nm. The small size of the nanoparticles indicates that these particles do not cause stress concentration and so they do not reduce the flexibility of the polymer matrix. The white areas in the TEM images indicate the presence of water molecules around the silica nanoparticles. The water molecules' accumulation represents that the silica nanoparticles are hydrophilic. Furthermore, the FTIR spectroscopy confirms the presence of water molecules. The results of the refractive index for different concentrations of the nanocomposite of PEG/SiO_2 are given in Figure 9.

Figure 9 shows the number of the refractive index of the nanocomposite. It is observed that the refractive index increases with increasing the concentration of OCAPS. Morever, less distance between the nanoparticles (OCAPS) and the more uniform distribution of OCAPS increase the refractive index. Thus, increasing the number of particles leads to the reduction of the distance between them, and then the refractive index of the nanocomposite increases. In addition, the small size of nanoparticles makes the light not disperse substantially, the optical transparence of the nanocomposite improves and the refractive index increases. Since the refractive index of the lens of the human eye is 1.411, achieving this refractive index is important. In this work, with the OCAPS with a concentration of 45%, the refractive index is close to that number.

The results of the transmission and absorption of light with respect to the nanostructured composite material of polyethylene glycol-silica are provided in Figure 10. UV absorption can be achieved by using Equation 2.

$$A = - Log (T\% / 100\%) \quad (2)$$

By placing the amount of light transmission in Equation 2, the absorption values are obtained. Figure 10 shows the results.

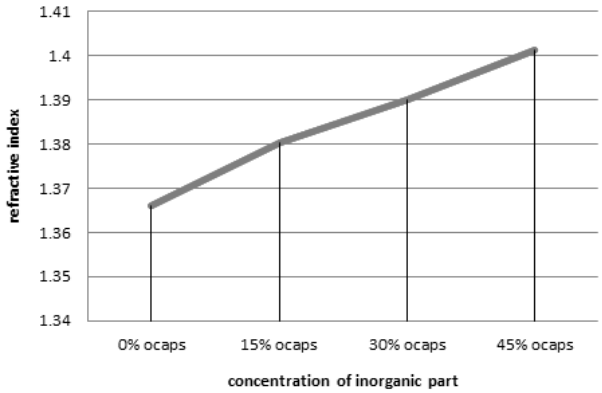

Figure 9. Changes in the refractive index of the nanostructured composite material of polyethylene glycol-silica versus the concentration of silica nanoparticles (accuracy 0.0002).

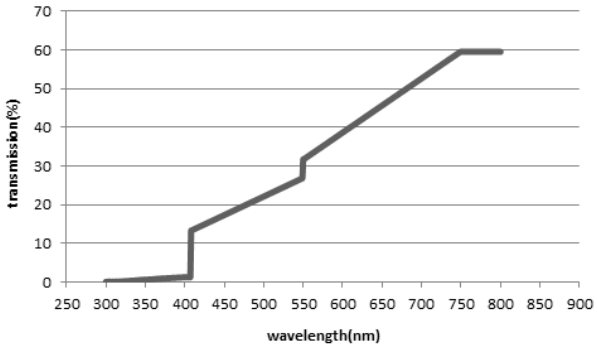

Figure 10. Percent change in the light transmission of the nanostructured composite polyethylene glycol-silica in the ultraviolet and visible.

Figures 11 and 12 show that the percentage of the passing of and the absorption of ultraviolet light by polyethylene the glycol-silica nanocomposite is very low and insignificant. This property is important for the use of intraocular lenses. It would look better if the hydrophilic nanocomposite overcame its hydrophobic portion. Thus, its transparency is closer to 100%. Furthermore, previously in the research of Kown [27], the material was used as an injectable intraocular lens and consisted of 70% hydrophilic hydrogel. However, it should be noted that overcoming the hydrophilic properties of nanocomposites must not change the amount of the other compound. In addition, the other factor that can affect the transparency of the nanocomposite is the crystallinity of the polymer. Generally, increasing the degree of the crystallinity of the polymer reduces light transmittance.

When the polymer chains are unable to reach an arrangement (woolen skein), this polymer is called formless (amorphous). The most important feature of these polymers is transparency, which is due to the transmission of light through their chains. Thus, the polymeric part of the prepared nanocomposite in this study consisted of polyethylene glycol, which has the property of crystallinity. It is likely to reduce light transmittance. Therefore, the polymer can be desirable in maintaining the hydrophobic nature and is preferably amorphous. Other important factors that can be very effective in reducing light transmittance are impurities and dust in the environment and laboratory equipment. Reducing transparency can be due to the accumulation of the polymer part of the prepared nanocomposite. In addition, the size of the nanoparticles can also be important in light transmittance. When the size of the particles is smaller, there is less light scattered, thus making the nanocomposite more optically transparent. The size of the nanoparticles used in this study is about 50-100 nm. Therefore, the transparency of the nanocomposite decreased slightly. The changes of modulus and loss modulus via temperature are shown in Figure 13. Also, Figure 14 shows that the increase in temperature reduces the viscosity of the material. When the temperature increases up to 40°C, the shear storage modulus and shear loss modulus are severely reduced. Relations between the storage modulus, loss modulus and tangent delta are shown in Figure 15.

$$G^* = G' + i\,G'' \quad (3)$$

$$Tan\,\delta = G' / G'' \quad (4)$$

$$i^2 = -1 \quad (5)$$

In these relationships, G^* [29] is the shear modulus. Complex viscosity (η^*) [29] depeneds on the storage modulus and loss modulus, and can be caculated by Equation 6.

$$\eta^* = (G' + i\,G'') / i\omega \quad (6)$$

In this equation, ω is the angular frequency and also $i = \sqrt{-1}$.

Figure 13 shows the changes in complex viscosity via temperature. It shows the reduction in viscosity with the increase in temperature.

It is noted that the storage modulus and loss modulus are functions of angular frequency (ω), which is the ratio of stress to maximum strain. The storage modulus and loss modulus are the elastic part and the viscous part, respectively. For chemical gels (strong gels), the storage modulus is less than the loss modulus ($G'<G''$), and for physical gels (weak gels), the storage modulus is usually greater than the loss modulus ($G'>G''$) [29].

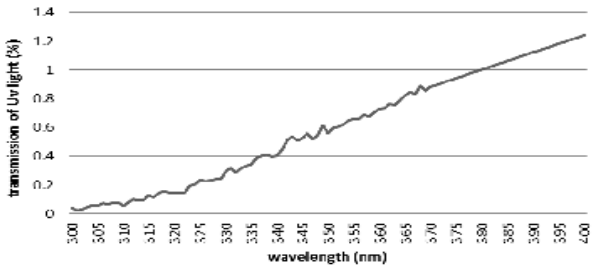

Figure 11. Percent change in light transmission of nanostructured composite polyethylene glycol - silica in the ultraviolet region.

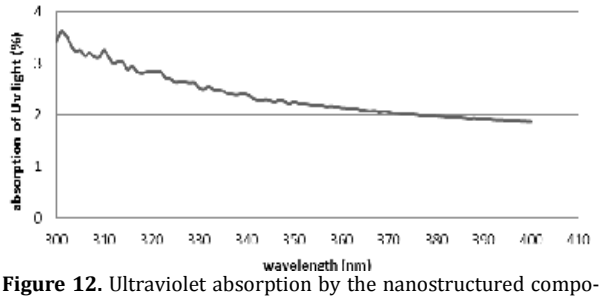

Figure 12. Ultraviolet absorption by the nanostructured composite material of polyethylene glycol - silica.

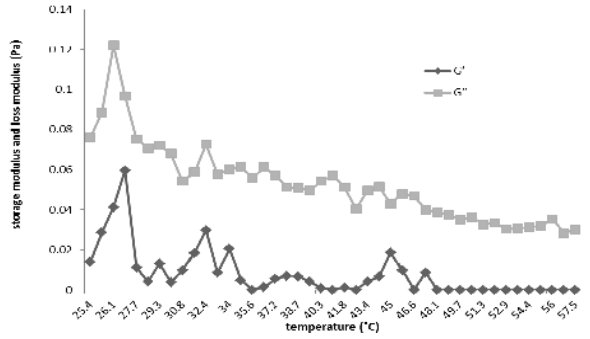

Figure 13. Changes in the storage modulus and loss modulus of the PEG/SiO_2 nanocomposite versus temperature.

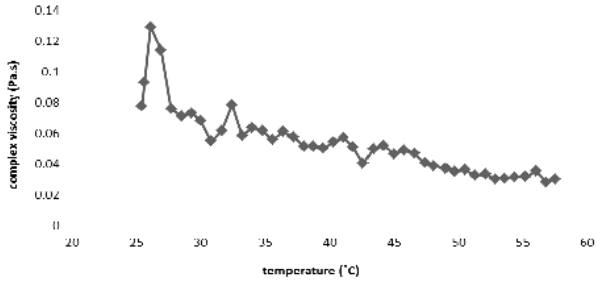

Figure 14. Changes in the complex viscosity of the polyethylene glycol-silica nanostructure composite versus temperature.

For fluid behavior in prepared nanocomposites, the storage modulus is less than the loss modulus, indicating that the material is a chemical gel. In the application of the ophthalomology lens, material is injected into the lens' capsular bag with a 27-gauge needle [3]. Synthesized nanocomposites become a gel at body temperature and fill the capsular bag completely [3, 27, 28]. Thus, nanocomposite material, which reduces its viscosity after warming, is easily injected. Reducing the temperature increases the storage and, thus, the elastic part increases. Therefore, the required elasticity will be retained.

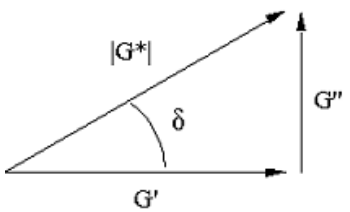

Figure 15. The vector display of relationship between the storage modulus, loss modulus and shear modulus.

4. Conclusion

In this study, the nanostructured composite material of polyethylene glycol-silica, using the silane coupling agent 3-aminopropyltrimethoxysilyl as a source of silica nanoparticles, was prepared in three steps. The results of small-angle and high X-ray scattering analysis confirmed that there is a amorphous silica phase in the nanocomposite. Furthermore, the presence of two sharp peaks indicated the crystallinity property of the polymeric in the nanocomposite. Morever, the presence of OH bonds in the FTIR spectra confirmed the hydrophilic property of silica nanoparticles. Also, the size of the silica particle in the polyethylene glycol-silica nanocomposite was estimated in the nanoscale range with the uniform distrubution in the polymer matrix. The measurement of the refractive index of the nanocomposite at various concentrations of OCAPS showed that by increasing the number of silica nanoparticles and reducing the distance between particles, doing this induced the enhancement of the refractive index. Finally, the appropriate concentration of OCAPS was determined to obtain the refractive index number of nanocomposite, which is closer to the natural lens of the human eye. Furthermore, results showed the reduction of the viscosity of nanocomposite with an increase in temperature, and when the low viscosity of a nanocomposite is induced, it is possible to inject it by syringe in medical applications.

Acknowledgment

Thanks to the NanoNafez Company, located in the Science and Technology Park of Semnan University, that collaborated on this study.

References

[1] Daniel-da-silva AL, Pinto F, Lopes-da-silva JA, Trindade T, Goodfellow BJ, Gil AM. Rheological behavior of thermo-reversible κ-carrageenan / nanosilica gels. *Colloid Interface Sci* 2008; 320: 365-614.
[2] Kango S, Kalia S, Celli A, Njuguna J, Habibi Y, Kumar R. Surface modification of inorganic nanoparticles for development of organic-inorganic nanocomposites - A review. *Prog Polym Sci* 2013; 38: 1232-1261.
[3] Annaka M, Mortensen K, Matsuura T, Nochiokad MIK, Ogata N. Organic-inorganic nanocomposite gels as an in situ gelation biomaterial for injectable accommodative intraocular lens. *Soft Mater* 2012; 8: 7185-7196.
[4] Nagarwal CR, Kant S, Singh PN, Maiti P, Pandit JK. Polymeric nanoparticulate system: A potential approach for ocular drug delivery. *J Control Rel* 2009; 136: 2-13.

[5] Hao X, Jeffery JL, Wilkie JS, Meijs GF, Clayton AB, Watling JD, Ho A, Fernandez V, Acosta C, Yamamoto H, Mohamed GM, Parel JM, Hughes TC. Functionalised polysiloxanes as injectable, in situ curable accommodating intraocular lenses. *Biomaterials* 2010; 31: 8153-8163.
[6] Nishi O, Nishi Y, Chang S, Nishi K. Accommodation amplitudes after an accommodating intraocular lens refilling procedure: In vivo update. *J Cataract Refract Surg* 2014; 40: 295-305.
[7] Assia E. Accommodative intraocular lens: A challenge for future development. *J Cataract Refract Surg* 1997; 23: 332-336.
[8] Colthurst MJ, Williams RL, Hiscott PS, Grierson I. Biomaterials used in the posterior segment of the eye. *Biomaterials* 2000; 21: 649-665.
[9] DeBoer C, Wan Do H, Lee J, Humayun M, Tai YC. **Biomimetic accommodating intraocular lens**. IEEE; 2012.
[10] Kayo ON, Nishi NY, Chang S. Capsular bag refilling using a new accommodating intraocular lens. *J Cataract Refract Surg* 2008; 34: 302-309.
[11] Reilly MA, Hamilton PD, Perry G, Ravi N. Comparison of the behavior of natural and refilled porcine lenses in a robotic lens stretcher. *Experim Eye Res* 2009; 88: 483-494.
[12] Nishi Y, Mireskandari K, Khaw P. Lens refilling to restore accommodation. *J Cataract Refract Surg* 2009; 35: 374-382.
[13] Nishi O, Nishi K, Mano C, Ichihara M, Honda T. Lens refilling with injectable silicone in rabbit eyes. *J Cataract Refract Surg* 1998; 24: 975-982.
[14] Hunter JJ, Melanie CW, Geraghty E. Optical analysis of an accommodating intraocular lens. *J Cataract Refract Surg* 2006; 32: 269-278.
[15] Vilupuru AS, Glasser A. Optical and biometric relationships of the isolated pig crystalline lens. *Ophthal Physiol Opt* 2001; 21: 296-311.
[16] Koopmans SA, Terwee T, Van Kooten TG. Prevention of capsular opacification after accommodative lens refilling surgery in rabbits. *Biomaterials* 2011; 32: 5743-5755.
[17] Koopmans SA, Terwee T, Hanssen A, Martin H, Langner S, Stachs O, Van Kooten TG. Prevention of capsule opacification after accommodating lens refilling: Pilot study of strategies evaluated in a monkey model. *J Cataract Refract Surg* 2014; 40: 1521-1535.
[18] Rana A, Miller D, Magnante P. Understanding the accommodating intraocular lens. *J Cataract Refract Surg* 2003; 29: 2284-2287.
[19] Entabi M, Harman F, Lee N, Bloom PA. Injectable, 1-piece hydrophilic acrylic toric intraocular lens for cataract surgery: Efficacy and stability. *J Cataract Refract Surg* 2011; 37: 235-240.
[20] Xu T, Jiaa Z, Luo Y, Jia D, Pengba Z. Interfacial interaction between the epoxidized natural rubber andsilica in natural rubber/silica composites. *Appl Surf Sci* 2015; 328: 306-313.
[21] Yousefpour MA, Taherian Z. The effects of ageing time on the microstructure and properties of mesoporous silica-hydroxyapatite nanocomposite. *Superlattices Microstruct* 2013; 54: 78-86.
[22] He L, Li J, Zhou C, Zhu H, Cao Z, Tang B. Phase change characteristics of shape-stabilized PEG/SiO2 composites using calcium chloride-assisted and temperature-assisted sol gel methods. *Solar Energy* 2014; 103: 448-455.
[23] Khanna L, Verma NK. Study on novel, superparamagnetic and biocompatible PEG/KFeO2 nanocomposite. *J Appl Biomedicine* 2014; 349: 116-120.
[24] Evora VMF, Shukla A. Fabrication, characterization, and dynamic behavior of polyester/TiO2 nanocomposites. *Mater Sci Eng A* 2003; 361(1-2): 358-366.
[25] Oh C, Ki CD, Chang JY, Oh SG. Preparation of PEG-grafted silica particles using emulsion method. *Mater Letters* 2005; 59: 929-933.
[26] Kiasat AR, Nazari S, Davarpanah J. Facile synthesis of an organic-inorganic nanocomposite, PEG-silica, by sol-gel method; its characterization and application as an efficient catalyst in regioselective nucleophilic ring opening of epoxides: Preparation of b-azido alcohols and b-cyanohydrins. *Chimie* 2014; 17: 124-130.
[27] Kwon JW, Han YK, Lee WJ, Cho CS, Paik SJ, Cho D, Lee JH, Wee WR. Biocompatibility of poloxamer hydrogel as an injectable intraocular lens. *J Cataract Refract Surg* 2005; 31: 607-613.
[28] Hao X, Jeffery JL, Tam PT, McFarland G, Johnson G, Mulder RJ, Garrett Q, Nankivil FMD, Arrieta E, Ho A, Parel JM, Hughes TC. High refractive index polysiloxane as Injectable, in situ curable accommodating intraocular lens. *Biomaterials* 2012; 33: 5659-5671.
[29] Kjoniksen AL, Nystro B, Lindman B. Dynamic viscoelasticity of gelling and nongelling aqueous mixtures of ethyl (hydroxyethyl) cellulose and an ionic surfactant. *Macromolecules* 1998; 31: 1852-1858.
[30] Qian T, Li J, Yang H. The preparationofagreen-shape-stabilized composite phase change material of polyethyleneglycol/SiO2 with enhanced thermal performance based on oil shaleash via temperature-assisted sol-gel method, *Solar Energy Mater Solar Cells* 2015; 132: 29-39.