A study on the optical properties of the PMMA polymer doped with some semi metal dioxides nanoparticles

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Abstract: This work on a compound polymer PMMA doped with some semi-metal oxides nanoparticles (SiO2, TiO2) NPs, intended to be utilized in corrective Contact Lenses. For this purpose the optical properties of the PMMA compound (PMMA+2%SiO2, PMMA+2%TiO2, and PMMA+1%SiO2+1%TiO2) NPs were measured and calculated to get the proper refractive indices and dispersion properties (Abbe number) for these compounds for optical design optimization.

Keywords: optical properties; PMMA polymer; nanoparticles

1- Introduction:
Polymeric materials constitute the most technically and economically important class of organic materials. Plastics, fibers, and the familiar biological materials surrounding us attest to this importance. These materials, which consist of repeating units known as "high polymers", are known [1]. Composite polymers of acrylates and methacrylates that contain sulfur have diverse advantages for applications in plastic lenses, optical fibers, and optical disc substrates [2]. Optical glass properties provide data of refractive indices over a wide range of successively used wavelengths and Abbe numbers at specific spectral lines as a measure of dispersion [3]. Nanoparticles with high refractive index can be incorporated into the polymer matrix to adjust the nanocomposites refractive index[4-6]. In the recent period, many polymers with high Abbe number and very high refractive index have been used[7-12]. The development of the (PMMA) in 1960s facilitate the employment of the plastic lenses and made them the first choice in corneal lenses manufacturing in spite of the major disadvantage, that is, the Oxygen impermeability at that time[6]. But in the later three decades Oxygen-permeable rigid materials were develop to get rid of this problem in the contact lenses (Cls). Therefore these polymers are referred to as rigid gas permeable (RGP) materials lenses. All the Cls types, sclerals, PMMAs, RGPs are referred to as (rigid) or (hard) Cls.

2- Theory:
The optical properties of any dielectric material mainly concern the behaviors of the optical beam propagation through the material and how this material interact with this electromagnetic wave.
The main material parameters rise from this interaction are absorbance, transmittance, reflectance, and the refractive index of the material, which manifest itself as the dispersive property of the material. All of these parameters may be measured and calculated through the well-known beer-lambert's relation:

\[ I = I_0 e^{-\alpha d} \]

Where \( I \) is the incident light beam, \( I_t \) is the transmitted light beam, \( \alpha \) is the absorption coefficient, and \( d \) is the material sample thickness (The average thickness of the sample is 540\( \mu \)m).

The transmittance of the sample is the ratio \( \frac{I_t}{I_0} = T \) the absorbance of the sample is defined as:

\[ A = \log \left( \frac{1}{T} \right) \]

And \( A \) is related to \( \alpha \) as follows

\[ \alpha = 2.303 \frac{A}{d} \]

The attenuation coefficient \( \alpha \) is the related to the imaginary part of the material complex refractive index as follows:

\[ \alpha = \frac{4\pi k}{\lambda} \]

\( K \) is the material extinction coefficient, and \( \lambda \) is the light beam wavelength

The real part of the complex refractive index is another important spectral parameter which indicates the dispersive characteristics of the material in terms of the Abbe number:

\[ V_d = \frac{(n_d - 1)}{(n_t - n_e)} \]

As long as part of the incident beam is absorbed, and the other part is transmitted then the conservation of energy principle dictate that third part is reflected off the sample surface. Hence

\[ A + T + R = 1 \]

Where \( R \) is the sample reflectance.

All of these parameters are spectral properties.

The relation between the refractive index and the reflectance may be given as:

\[ n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \]

3- **Experimental:**

The PMMA powder, was dissolved in chloroform. The PMMA then doped with SiO2, TiO2, ZnO, SiO2+ZnO, and SiO2+TiO2 nanoparticles. The nanoparticles size ranges between (20-30 nm). The NPs powder was mixed in the PMMA solvent in the stirrer device. The casting method
was used to prepare samples at room temperature. An ultrasound generator is used to break up the clusters in the nanopowders powder.

4- Results and Discussion:

The dispersion relation is calculated and manifested in Fig.(4). The Abbe number is a function for the dispersive power of the optical material and it’s values for certain standard wavelengths (486, 58, and 656 nm) are shown in Table (1). The low values of the refractive indices differences indicates the relatively low dispersive power for the polymer with its additives (SiO2+TiO2 NPs) and (SiO2 + ZnO NPs). This is an important result for the purpose of contact lens design since it reduces the chromatic aberration.

Table (1): Shows Abbe number of all prepared samples

| System          | n_486  | n_587  | n_656  | V_d   |
|-----------------|--------|--------|--------|-------|
| PMMA 100%       | 1.891659937 | 1.877483827 | 1.871049094 | 42.573 |
| PMMA + 2% SiO2  | 1.905780247 | 1.897412264 | 1.886893696 | 47.515 |
| PMMA + 2% TiO2  | 2.590691372 | 2.62821499  | 2.562838337 | 58.457 |
| PMMA + 1% SiO2 + 1% TiO2 | 2.604002211 | 2.587694167 | 2.564352516 | 40.043 |

**Figure 1.** shows the relationship of the Absorbance with the wavelength of the prepared nanocomposite

**Figure 2.** shows the relationship of the Transmittance with the wavelength of the prepared nanocomposite
AFM analysis was performed to study the surface topography or the surface roughness values of the samples. The following figures show the AFM images for the prepared samples. The brightest region represents the highest point of the sample surface, while the darker region shows the deepest point of the sample.

Figure 3. shows the relationship of the Reflectance with the wavelength of the prepared nanocomposite

Figure 4. shows the relationship of the Refractive index with the wavelength of the prepared nanocomposite

Figure 5. An atomic force microscope image of a PMMA sample is represented as a two-dimensional and three-dimensional image with a resolution of 50 μm.
Figure 6. The atomic force microscope image of a two- and three-dimensional PMMA + 2% SiO2 sample with a resolution of 50 μm.

Figure 7. The atomic force microscope image of a two- and three-dimensional PMMA + 2% TiO2 sample with a resolution of 50 μm.
Figure 8. The atomic force microscope image of a two- and three-dimensional PMMA +1%SiO2 +1% TiO2 sample with a resolution of 50 μm.

The X-ray diffraction technique was used to study the crystal structure of samples (PMMA), (PMMA / SiO2), within the angular range (2θ = 8° - 82°), and from the assay application of the (PMMA) polymer, at room temperature. Three peaks appear at the corners (14.07, 30.34, 41.97), as in Figure (9), which indicate the random nature of the sample (amorphous) [7].

When applying the test for (PMMA / SiO2), a single peak appears at the angle (13.52°), which indicates the presence of SiO2 compound, as shown in Figure (10).

When applying the test for (PMMA / TiO2), five peaks appear at the corners (21.27, 25.30, 27.28, 29.86, 31.27), as shown in Figure (11).

When applying the assay to a superposition (PMMA / SiO2 / TiO2), five peaks appear at the corners (14.94°, 17.30°, 19.22°, 20.39°, 79.67°) denoted Angles contain two elements (SiO2, TiO2) within the complex. As in Figure (12).
The crystal size was measured using the (Scherrer Equation) equation (to calculate the minute volume according to the following equation [15]: -

\[ D = \frac{K\lambda}{\beta_{hkl}\cos(\theta)} \]  

Where, \( \lambda \) is the x-ray wavelength (0.154 nm), \( \theta \) is the Bragg diffraction angle, and \( \beta \) is the full width at half maximum, (K) Constant and equal to 0.94.

**Table 2.** shows the average particle size of the PMMA polymer according to Scherer's equation

| \( \beta \) (deg) | \( \beta \) (rad) | \( 2\theta \) (deg) | \( \Theta \) (deg) | \( \theta \) (rad) | \( \cos(\theta) \) | \( D \) (nm) | \( D_{ave} \) (nm) |
|------------------|------------------|---------------------|-------------------|------------------|----------------|------------|---------------|
| 6.289983         | 0.10973          | 14.07               | 7.035             | 0.122775         | 0.992473       | 1.328725   |               |
| 2.943705         | 0.05134          | 30.34               | 15.17             | 0.264747         | 0.965159       | 2.919511   | 2.7928296     |
| 2.150932         | 0.03758          | 41.97               | 20.95             | 0.36623          | 0.933684       | 4.130253   |               |

When applying the test for (PMMA / SiO2), one vertex appears at the angle (13.5 °), which indicates the presence of SiO2 compound, as shown in Figure (8), According to the card (45-0131) SiO2.

**Table 3.** shows the average particle size of the PMMA+2%SiO2 polymer according to Scherer's equation

| \( \beta \) (deg) | \( \beta \) (rad) | \( 2\theta \) (deg) | \( \Theta \) (deg) | \( \theta \) (rad) | \( \cos(\theta) \) | \( D \) (nm) |
|------------------|------------------|---------------------|-------------------|------------------|----------------|------------|
| 6.544917         | 0.114222         | 13.52               | 6.76              | 0.117976         | 0.993049       | 1.272482   |

**Table 4.** Shows the presence of SiO2 in the compound

| \( 2\theta \) (deg) | ( hkl ) | n.of card |
|---------------------|---------|-----------|
| 13.52               | ( 200 ) | (45-0131) SiO2 |
Table 5. shows the average particle size of the PMMA+2%TiO2 polymer according to Scherer's equation

| θ (deg) | θ (rad) | θ (deg) | θ (rad) | COS (θ) | D (nm) | D_{ave} (nm) |
|---------|---------|---------|---------|---------|--------|-------------|
| 532.46 | 0.07218 | 21.47   | 10.735  | 0.187347| 0.982502| 2.0055      |
| 3.518091 | 0.061398 | 25.3    | 12.65   | 0.220768| 0.97573 | 2.35777     |
| 3.266411 | 0.057005 | 27.28   | 13.64   | 0.238045| 0.971801| 2.53965     |
| 2.990142 | 0.052184 | 29.86   | 14.93   | 0.260558| 0.966246| 2.7742      |
| 2.857743 | 0.049873 | 31.27   | 15.635  | 0.272862| 0.963004| 2.90263     |

Table 6. Shows the presence of TiO2 in the compound

| 2θ (deg) | ( khl ) | n.of card |
|---------|---------|-----------|
| 25.3    | ( 111 ) | 46-1238   |
| 27.28   | ( 111 ) | 46-1238   |
| 29.86   | ( 111 ) | 46-1238   |

During the crystallographic bending process, the material did not reach the bending temperature or any condition was not at the required level, except that some of the crystalline trends of TiO2 appeared, for example at the corners (25.3°, 27.28°, 29.86°) according to The Card (46-1238).

Table 7. shows the average particle size of the PMMA+1%SiO2 +1%TiO2 polymer according to Scherer's equation

| θ (deg) | θ (rad) | θ (deg) | θ (rad) | COS (θ) | D (nm) | D_{ave} (nm) |
|---------|---------|---------|---------|---------|--------|-------------|
| 63.36253 | 0.103406 | 14.94   | 7.47    | 0.130366| 0.991514| 1.42738     |
| 63.23966 | 0.089365 | 17.3    | 8.65    | 0.15096 | 0.988627| 1.6199      |
| 53.7248  | 0.085023 | 19.22   | 9.61    | 0.167714| 0.985969| 1.79775     |
| 53.4624  | 0.075939 | 20.39   | 10.195  | 0.177923| 0.984213| 2.49853     |
| 1.20245  | 0.020985 | 79.67   | 39.835  | 0.695201| 0.767925| 6.8989      |

Table 8. Shows the presence of SiO2 +TiO2 in the compound

| 2θ (deg) | ( khl ) | n.of card |
|---------|---------|-----------|
| 14.94   | ( 200 ) | (45-0131) SiO2 , (46-1238) TiO2 |
| 17.3    | ( 040 ) | (44-1394) SiO2 |
| 19.22   | ( 310 ) | 44-1394 SiO2/ |
| 20.39   | ( 041 ) | 44-1394 SiO2/ |
| 79.67   | ( 515 ) | (46-1238) TiO2 |
5- Conclusions:
The results of the XRD shows the amorphous nature of the polymer PMMA, and confirmed the existence of the SiO2 NPs within the matrix of the polymer composite. The composite film of PMMA-SiO2 NPs shows excellent optical transparency and low differences values for the refractive indices, which means low dispersive power optical material and hence it produces low chromatic aberration.

6- References:
[1] Ahmad, A. H., and A. M. Awatif. "Doping effect on optical constants of polymethylmethacrylate (PMMA)." Engineering and Technology Journal 25.4 (2007).
[2] Maheswara, Muchchintala, et al. "High refractive index of transparent acrylate polymers functionalized with alkyl sulfur groups." Polymer journal 42.3 (2010): 249-255.
[3] Sultanova, Nina, S. Kasarova, and Ivan Nikolov. "Dispersion proper ties of optical polymers." Acta Physica Polonica-Series A General Physics 116.4 (2009): 585.
[4] Guo, Qingchuan, et al. "Comparison of in situ and ex situ methods for synthesis of two-photon polymerization polymer nanocomposites." Polymers 6.7 (2014): 2037-2050.
[5] Cai, Bin, Toshikuni Kaino, and Okihiro Sugihara. "Sulfonyl-containing polymer and its alumina nanocomposite with high Abbe number and high refractive index." Optical Materials Express 5.5 (2015): 1210-1216.
[6] Lina M Shaker, Ali H. Al-Hamdani Ahmed A. Al-Amiery," Plastic Materials for Modifying the Refractive Index of Contact Lens: Overview , Res Dev Material Sci. 11(2), Research and development in material science, DMS.000760.2019
[7] Ali H. Al-Hamdani.Lina M. Shaker, Ahmed A. Al-Amery." Investigation of a high refractive index polymer for contact lens applications: Overview." Journal of engineering and applied sciences, 14 (Special Issue 7): 10052-10057, 2019.
[8] Lina M. Shaker, Ali H. Al-Hamdani, Ahmed a. Al-Amiery, " Nano-particle doped polymers to improve contact lenses optical quality, International Journal of Nanoelectronics and Materials Volume 13, No. 1, Jan 2020 (19-30)
[9] [9] Pablo Artal Editor ,Handbook of visual Optics ,Instrumentation and vision correction , Vol.2 , CRC Press , 2017
[10] Zahraa M. AL-Asady, Ali H. Al-Hamdani," Diffraction rings pattern and nonlinear optical properties for hybrid ZNO-NP / epoxy resin, Engineering and Technology Journal, Vol. 38, Part A (2020), No. 03, Pages 440-445.
[11] Ali H. Al-Hamdani, Improving Quality of Image Vision Using Aspherical Polysulfones Contact Lens. AIP Conference Proceedings 2213, 020070 (2020); https://doi.org/10.1063/5.0000260
[12] Zahraa M. AL-Asady Ali H. AL-Hamdani, Mohammed A. Hussein," Study the Optical and Morphology Properties of Zinc Oxide Nanoparticles, AIP Conference Proceedings 2213, 020061 march(2020); The 2nd International Conference on Materials Engineering and Science -University of Technology Baghdad-Iraq.
[13] Ali. H. Al-Hamdani. Design and performance analysis of contact lens materials for chromatic and polychromatic aberrations correction, Engineering and Technology journal, vol.36, part A, no.9 (2018)1016-1021.
[14] Al-Ammar, Khalid, Ahmed Hashim, and Maithem Husain. "Synthesis and study of optical properties of (PMMA-CrCl2) composites." Chem. Mater. Eng 1.3 (2013): 85-87.
[15] Salam Hussein Ewaid et al 2021 IOP Conf. Ser.: Earth Environ. Sci. 790 012075
[16] Salam Hussein Ewaid et al 2020 J. Phys.: Conf. Ser. 1664 012143.
[17] Ewaid, S.H.; Abed, S.A.; Al-Ansari, N.; Salih, R.M. Development and Evaluation of a Water Quality Index for the Iraqi Rivers. Hydrology 2020, 7, 67.
[18] Rameshkumar, C., et al. "Preparation and Characterization of Pristine PMMA and PVDF Thin Film Using Solution Casting Process for Optoelectronic Devices." J. Surf. Sci. Technol 33 (2017): 12-18.
[19] Ali, W., & R.Anon, M. (2020). Biological Effective of organic solvent extracts of Mirabilis jalapa Leaves in the Non-cumulative for mortality of Immature stages Culex quinquefasciatus Say ( Diptera : Culicidae ). Al-Qadisiyah Journal Of Pure Science, 25(1), Bio 1-6.
[20] Sami Abdi, mohammed, Shaker Hussein, A., & mohammed hadi, H. (2020). Study The Current Density-Voltage (J-V) Characteristics of α-Fe2O3 Thin Film Prepared by Spray Pyrolysis Technique. Al-Qadisiyah Journal Of Pure Science, 25 (1), Phys 1-7.