

# ATR-FTIR, SAXS and UV-vis studies of silicone hydrogel and bio-hydrogel soft contact lenses

## ABSTRACT

### Aims:

- compare micro/nano structures and determine UVA and visible light transmittance of the commercially available daily wear silicone hydrogel (SiHy) and bio-hydrogel (bio-Hy) soft contact lenses *in vitro*.
- estimated water content and investigated the effect of air-drying on the water content
- evaluated for ultraviolet (UV) and visible light (Vis) transmittance with and without UV filter and to compared with any claims made by the manufacturer.

**Place and Duration of Study:** Hacettepe University, Department of Physics, Ankara, Turkey, between May 2018 and May 2021.

**Methodology:** Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectra of CLs were recorded (at removing from its *package*, after 10 min, 1 h and 1 day at room temperature) in the region of 4000-650  $\text{cm}^{-1}$  to estimate water contents of CLs. Hierarchical Cluster Analysis (HCA) was performed to differentiate chemical structure of CLs based on the spectral differences. Small Angle X-ray Scattering (SAXS) analyses were performed to obtain further structural information on nano-scale. The optical transmission and reflection in the range from 315 to 800 nm were measured.

**Results:** One of the key observations in this study is the large influence of lens water content. The HCA analysis grouped all the CLs of same brand in same cluster based on their chemical similarity. The experimental UV results showed that all claims of the manufacturers for Class 1 or Class 2 were almost valid. The size (11.8-39.9 nm) and differences in morphologies of the nano globules were determined and correlated with equilibrium water content (*EWC*).

**Conclusion:** This work was designed to explain important characteristics of commercial CLs and results will have implications for future experimental and clinical research regarding hydration/ dehydration experiments with CL polymers.

**Keywords:** [Soft Contact Lenses, Lens polymers, Water content, ATR-FTIR, HCA, UV-vis, SAXS]

## 1. INTRODUCTION

Hydrogels (Hy) are commonly used for the manufacture of soft conventional and disposable contact lenses. Soft contact lenses are primarily made from hydrogel or silicone hydrogel material.

The silicone hydrogel lenses (SiHy-CLs) which provides easy adaptability to the eye and allow much more oxygen to pass through to the cornea than previous soft lens materials are the largest proportion of CLs on the market today. They are widely used in an active lifestyle due to their excellent biocompatibility, comfort and optic transparency [1–8].

SiHy-CLs combine silicone based / an extremely plastic flexible hydrophobic/materials and various hydrophilic monomers/polymers such as polyvinylpyrrolidone (PVP), used to increase the surface hydrophilicity of silicone. The bulkiness of the siloxane group and high polymer chain mobility induce the high oxygen permeability of these materials [8–13]. Nowadays, over 12 different SiHy materials are available in the marketplace that are named according to the criteria of the United States Adopted Names Council (USAN). The polymerization conditions/synthesis, manufacturing processes can be altered to produce the same polymer with different properties of CLs such as wear time and comfort [8,14–16].

Water content (WC) in contact lenses is the most important lens characteristics varies depending on the type of lens and effect vision and comfort. In soft CLs, the water content ranges from 38 to 75 % that has been approved by the FDA. The most common ways of measuring WC of soft lenses are by refractometry or gravimetry [17,18]. The contact lenses is strongly influenced by dehydration and this can induce changes in oxygen permeability (Dk), oxygen transmissibility (Dk/t), surface wettability or other lens parameter Differential scanning calorimetry, differential thermal analysis, sorption/desorption experiments Raman Spectroscopy, Near IR and ATR-FTIR spectroscopy have been used to better understand hydration properties of soft contact lenses [19–23].

ATR-FTIR spectroscopy is one of the fast, non-destructive, inexpensive and effective techniques in monomer-polymer analysis. It is also a powerful method to gain structural information on hydrated biological materials. In order to evaluate the differences and similarities among samples, unsupervised techniques such as hierarchical cluster analysis (HCA) can be made statistically based on the infrared spectral data set when the exact chemical components and the amounts of each are unknown in samples [24].

Exposure to UV radiations is the a risk factor and associated with ocular diseases, such as cataracts and macular degeneration [25–31]. The commercial CLs can have UV- protection or some offer limited to no UV-protection. The amount of UV absorbed or transmitted by contact lenses varies markedly between brands depending on manufacturer and lens material. It can even vary within the same manufacturer [5,32–41].

UV radiation spectrum is divided into three regions according to their wavelength called UVC (200-280 nm), UVB and UVA (315-380 nm). According to standard (Z80.20) set by the American National Standards Institute (ANSI), Class I contact lenses block 99% UVB and 90% UVA while Class II contact lenses block 95% UVB and 70% UVA. The spectral transmittance/reflectance properties in the visible region (400-700 nm) are also strongly dependent on the lens material and very important for visual performance.

The refractive index (RI) of a soft contact lens is an important physical parameter that effects the lens design and also indirect measure of its equilibrium water content (EWC) [42–46]. RI index can measure with automated and manual refractometer [46–48]. In the present study RI values of CLs were not measured directly but derived from transmittance/reflectance spectral measurements.

SAXS is a non-destructive and highly popular method to study the nanoscale structure of any type of material, ranging from new composite nanosystems to biological macromolecule. The chemical nature of the selected monomers and their compositions of the CLs materials can have effect on the nanoscale structure within the material. A more comprehensive understanding of the relationships between chemical properties and the material structures of CLs needs to be established [49,51].

The first purpose of the present work is to estimate the water content and the variation in water content with time of different brands SiHy and bio-Hy CLs by ATR-FTIR spectroscopy and discrimination of brands/ CL materials by HCA based on ATR-FTIR spectra. The second purpose of this study is to compare the UVA and visible transmittance characteristics (315-800 nm) of new and different CLs with and without UV filters.

To date, no SAXS studies have elucidated in detail. In the present study, 3D nano sizes and nanoscale morphologies of all CLs from different brands were probed. The results are used in order to find relation with the some important properties such as ECW and RI values of the CLs.

## 2. MATERIAL AND METHODS

Only new, unworn daily wear contact lenses were used in the present study. The commercially available 8 brands spherical SiHy, 2 brands spherical bio-Hy and 3 brands toric SiHy, contact lenses were obtain optician shop ( 6 lenses per box) in Turkey.

The manufacturer, brand and soft contact lens details with the claims of the manufacturers are specified in Table 1. An optical lens power of -2.00 and -4 diopters (D) were selected for each spherical lens brand, which are specified by the ANSI standard.

**Table 1. Properties of conventional soft contact lenses used in this study**

Manufacturer	Brand name	Material (USAN)	Principle Monomer and polymer*	EWC (%)	Dk/t	RI	Transmission (%)	
							Light	UVB/UVA
CooperVision Hamble, UK	Biofinity	Comfilcon A 52 %	NVP, VMA, IBM, TAIC, M3U, FM0411M, HOB	48	160	1.40	>97	
Bausch & Lomb Inc.,	Pure Vision 2	Balafilcon A	A silicone vinyl carbamate, a	36	130	1.426	95	

Rochester, NY, USA	PWR :-2/-4	64%	siloxane crosslinker and a vinyl alanine wetting monomer				
Alkon-USA Made in Malaysia <i>Only for sale in Turkey</i>	Air Optix Aqua PWR :-2/-4	Lotrafilcon B 67 %	Siloxane, DMA, TRIS	33	138	1.42	96 at 610 nm
Alkon-USA Made in Indonesia <i>Only for sale in Turkey</i>	Air Optix Nigth & Day PWR :-2/-4	Lotrafilcon A 76%	Siloxane DMA, TRIS	24	175	1.43	-
Interjo Inc Gyeonggi-do, Korea	Elegance Comfort PWR :-2/-4	Innofilcon A 55 %	-	45		-	-
Bausch & Lomb Inc., Rochester, NY, USA	Ultra with Moisture Seal PWR :-2/-4	Samfilcon A 54 %	Siloxane Methacrylate, NVP	46	163	1.411	≥ 95%
Johnson & Johnson Vision Care- Ireland <b>UV Blocking</b>	Acuvue Oasys with Hydraclear® Plus PWR: -2/-4	Senofilcon A 62%	-	38	147	1.42	UVB: less than 1% in UVA :less than 10%
Cooper Vision Scottsville, NY USA <b>UV Blocking</b> <b>Bio- Hydrogel Contact Lenses</b>	Avaira Vitality PWR: -2	Fanfilcon A 45 %	-	55	110	1.398	: 98% +2/-5% 1% UVB 10% of UVA
Wöhlk Contaklinsen GmbH Germany <b>UV Blocking</b>	Contact Life PWR :-2/-4	Vitafilcon A 46%	-	54	20		-
Wohlk Contaklinsen GmbH Germany <b>UV Blocking</b>	ZEISS Contact Day PWR :-2/-4	Ocufilcon F %45	-	55	19		-

Table 1 (Continue)

Manufacturer	Brand name	Material (USAN)	Principle Monomer and polymer*	EWC (%)	Dk/t	RI	Transmission (%) Light UVB/UVA
<b>Toric (for astigmatism) Lenses</b>							
CooperVision Hamble, UK	Biofinity SPH -1 CLY -0,75	Comfilcon A 52 %	NVP, VMA, IBM, TAIC, M3U, FM0411M, HOB	48	116		97

Bausch & Lomb Inc., Rochester, NY, USA	AX 180 Pure Vision 2	Balafilcon A 64 %	A silicone vinyl carbamate, NVP, a siloxane crosslinker and a vinyl alanine wetting monomer	36	91	1.426	≥ 95%
	SPH -1 CLY -0,75						
Johnson & Johnson Vision Care Ireland	Acuvue Oasys with HYDRACL EAR <sup>®</sup> PLU S	Senofilcon A 62%	-	38	129.3	-	UVB: less than 1% in UVA :less than 10%
<b>UV Blocking</b>	SPH -1 CLY -0,75 AX 180						

- (not claim)

Abbreviations.

USAN: United States Adopted Names, RI: Refractive index, EWC : The equilibrium water content, SPH: sphere – myopic, CYL: Cylinder , AX: Axis.

DMA (N,N-dimethylacrylamide); EGDMA (ethyleneglycol dimethacrylate); FM0411M (2-ethyl [2-[(2-methylprop-2-enoyl)oxy]ethyl]carbamate); HOB ((2RS)-2-hydroxybutyl 2-methylprop-2-enoate); IBM (Isobornyl methacrylate); M3U ( $\alpha$ -[[3-(2-[[2-(methacryloyloxy)ethyl]carbamoyloxy]ethoxy)propyl]dimethylsilyl]- $\omega$ -[3-(2-[[2-(methacryloyloxy)ethyl]carbamoyloxy]ethoxy)propyl]poly[[oxy[(methyl) [3-[ $\omega$ -methylpoly(oxyethylene)oxy]propyl]silylene]/[oxy[(methyl)(3,3,3trifluoropropyl)]silylene]/oxy (dimethylsilylene)]]); NVA (N-vinyl aminobutyric acid); NVP (N-vinyl pyrrolidone); PBVC (poly[dimethylsiloxy] di [silybutanol] bis[vinyl carbamate]); PVP (poly(vinylpyrrolidone)); TAIC (1,3,5-triisoprop-2-enyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione); TPVC (tris-(trimethylsiloxy)silyl propylvinyl carbamate); VMA (N-Vinyl-N-methylacetamide); TRIS 3- (methacryloyloxy)propyltris(trimethylsiloxy)silane

## 2.1 ATR-FTIR Spectra

ATR-FTIR spectra were recorded using a Perkin Elmer Spectrum 100 FTIR spectrometer with a Universal diamond ATR accessory. 32 scans were performed for all measurements with a resolution of 4 cm<sup>-1</sup> in the 4000-650 cm<sup>-1</sup> spectral region. Six soft contact lenses from each brand were used and then three measurements (immediately removed from package, under air-dried after 10 min, 1 h and 1 day) were made on each sample to check the reproducibility of the identical spectra.

All raw spectra are converted from transmittance to absorbance and no ATR baseline correction was applied. The average spectrum was taken for each sample and then was smoothed using a Savitzky-Golay filter (smoothing points: 13) using the OPUS 5.5 software package (Bruker Optics GmbH, Ettlingen, Germany).

The absorbance spectra were then baseline corrected and then normalized with respect to CH<sub>2</sub>-CH<sub>3</sub> stretching region (3020-2800 cm<sup>-1</sup>) for visual demonstration of the spectral differences in the spectra of studied CLs. To estimate water content of CLs of different brands the band area under the 3700–3020 cm<sup>-1</sup> region was integrated.

Spectral differentiation of different brand CLs, HCA analysis was performed using OPUS 5.5 software. Vector normalized, second derivative of each spectrum in the range of 4000–650

$\text{cm}^{-1}$  was used as an input data. Spectra were smoothed using 13-points. The dendrogram was calculated using Ward's method and Euclidean distances.

## 2.2 UV-VIS Measurement

Computer controlled monochromator (CVI Digichrome 240 with a focal length of 20 cm) operating with the spectral range from 315 to 800 nm at 2 nm intervals and a BPW34 photodiode were used for measurements transmittance (T) and reflection (R).

Two measurements were made on each sample to check the reproducibility of the identical spectra.

## 2.3 SAXS Measurement

SAXS experiments were performed with Kratky compact HECUS system (Hecus X-ray systems, Graz, Austria) equipped with a linear collimation system and X-ray tube with a Cu target ( $\lambda = 1.54\text{\AA}$ ). The generator was operated at a power of 2 kW (50 kV and 40 mA).

Scattering intensity  $I(q)$  is plotted against  $q$ - magnitude of the scattering vector. The PDDs were adjusted to be the smallest chi-square ( $\chi^2$ ) value, and 3D morphologies of electron density of CLs were found in the DAMMIN program [52–54].

## 3. RESULTS AND DISCUSSION

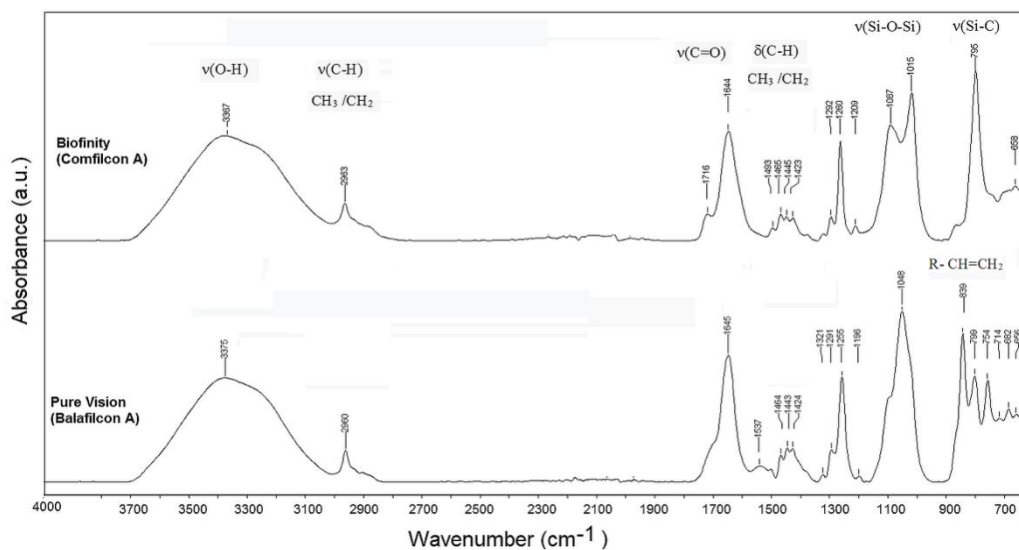
### 3.1 ATR-FTIR and HCA Analyses

The CL materials used in this study are composed of 10 polymeric materials (Comfilcon A, Balafilcon A, Innofilcon A, Lotrafilcon A, Lotrafilcon B, Samfilcon A, Senofilcon A, Fanfilcon A, Vitafilcon A and Ocufilecon F) with different contents and amounts. The most important factor in these lenses is the amount of carbon, oxygen, nitrogen and silicon (for SiHy). In addition, Lotrafilcon A and Lotrafilcon B contain fluorine, unlike the others. A very small amount (0.61%) of fluorine has reported in Biofinity-Comfilcon A [55].

Poly dimethylsiloxane (PDMS) and /or 3-(methacryloyloxy) propyltris(trimethylsiloxy) silane (TRIS) macromonomers are the most important components in silicone hydrogel contact lenses.

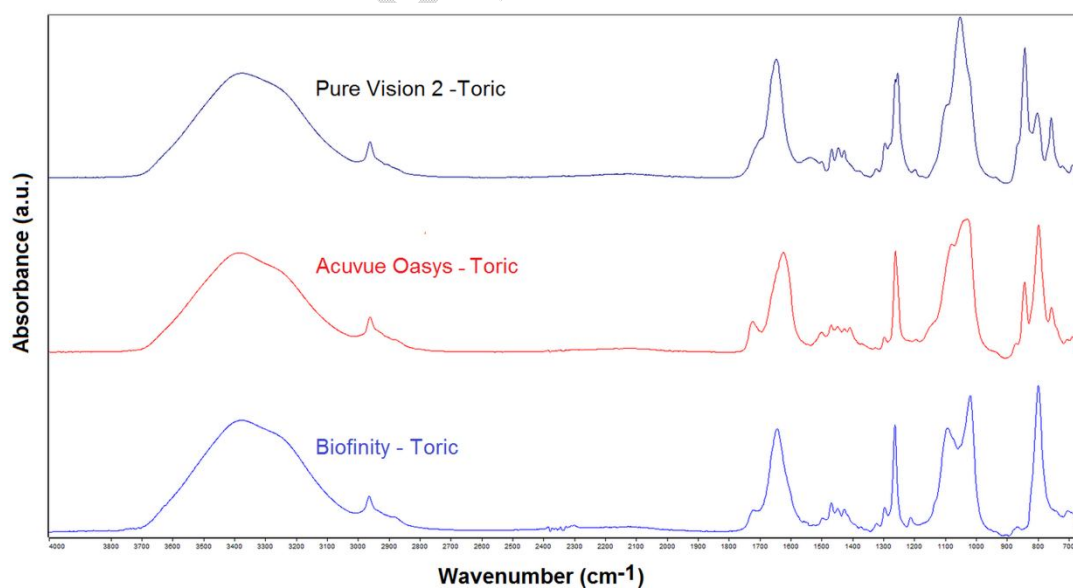
The characteristic vibrational bands in the ATR-FTIR spectra of pure PDMS and TRIS are the C-H stretching and the deformation modes of the Si-CH<sub>3</sub> group between 2950-2960  $\text{cm}^{-1}$  and strong sharp band at around 1260  $\text{cm}^{-1}$ , respectively. Si-O-Si stretching in the range of 1020-1075  $\text{cm}^{-1}$  and Si-C stretching in the range of 760-800  $\text{cm}^{-1}$ . Methyl methacrylate (CH<sub>2</sub>=C(CH<sub>3</sub>)COOCH<sub>3</sub>) group of TRIS exhibit C=O and C-O-C stretching bands at around 1725  $\text{cm}^{-1}$  and 1145  $\text{cm}^{-1}$ , respectively.

Vibrational bands related to O-H, N-H, CH<sub>2</sub>N-C, C=O, C-O and R-CH=CH<sub>2</sub> groups in hydrophilic monomers used in a soft SiHy CLs can also be observed in the infrared spectra. The ATR-FTIR spectra of -2 and -4 powered lenses appear quite similar. Representative ATR-FTIR spectra with assignments for the main bands for Biofinity contain Comfilcon A and PureVision2 contain Balafilcon A with lens power - 2 are given in Fig. 1.



**Fig. 1. Representative ATR-FTIR spectra with assignments for the main bands of spherical SiHy CLs of Biofinity and PureVision2.**

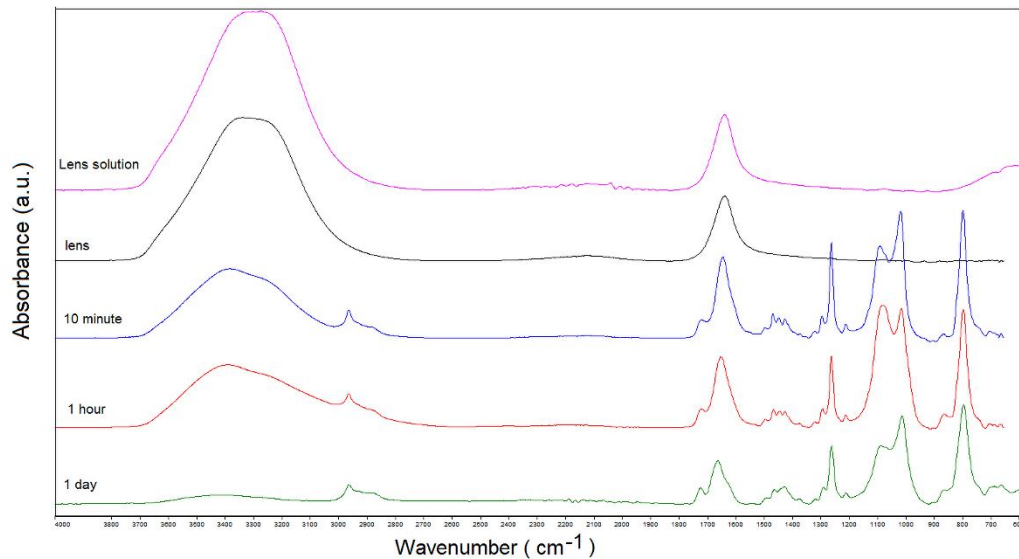
ATR-FTIR spectra of the toric lenses of 3 brands (Biofinity, Acuvue Oasys and Pure Vision2 with Comfilcon A, Balafilcon A, and Senofilcon A copolymers, respectively) are given in Fig. 2. There is no differences in the ATR-FTIR spectra of spherical and toric lenses of same brand.



**Fig. 2. Average ATR-FTIR spectra of toric SiHy CLs of Biofinity, Acuvue Oasys and Pure Vision2.**

The O-H stretching band in the  $3700\text{--}3050\text{ cm}^{-1}$  were associated to general intramolecular and intermolecular hydrogen bonding and to free hydroxyl in lens material. This band is also representative of the contribution of the free or the bound water linked to the substrate. It can be used to describing the hydration process [56–58].

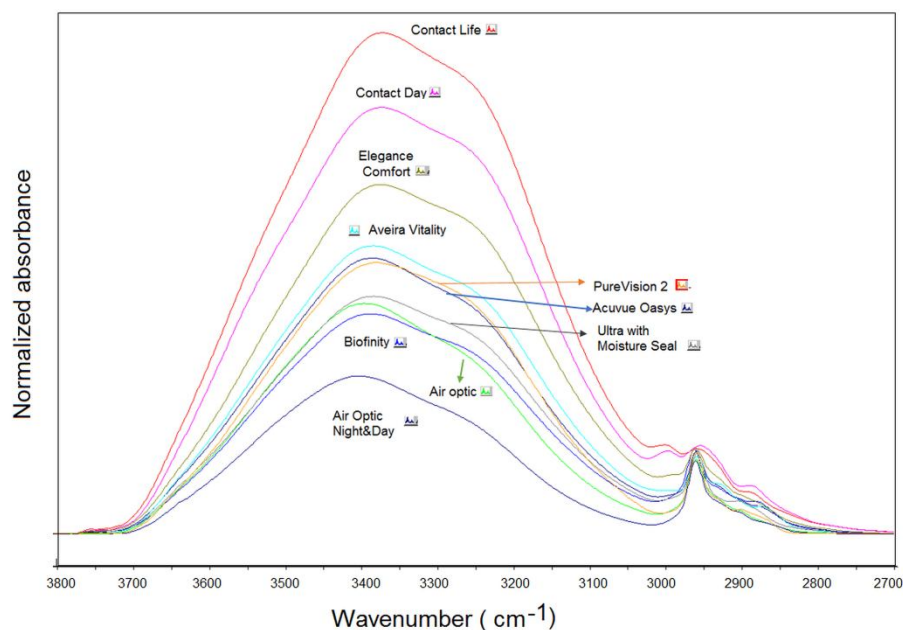
Since the high water content in the packaging solution, a strong broad absorption band exhibit  $\nu$  (O-H), stretching vibration in the range of  $3700\text{--}3020\text{ cm}^{-1}$  in the ATR-FTIR spectra. Fig. 3 shows the average ATR-FTIR spectra of spherical lenses of Biofinity brand (as a representative) immediately removed from package, under air-dried after 10 min, 1 h and 1 day and its packaging solution for comparative purpose.



**Fig. 3. Time evaluation of the average ATR-FTIR spectra of spherical SiHy CLs of Biofinity brand and buffered saline as package lens solution.**

Band intensities of O-H stretching band decreased and intensities of some band of functional groups of lens material increased due to decrease water content of the lenses, which started to dry.

The intensity of water bands in infrared spectra is actually an indicator of the water content in the lens material. Fig. 4 shows comparative infrared spectra after 10 min of the spherical CLs from 10 brands in the  $3800\text{--}2700\text{ cm}^{-1}$  region.



**Fig. 4. Comparative normalized average ATR-FTIR spectra after 10 minutes of the ten spherical contact lens brands in 3800-2700  $\text{cm}^{-1}$  region.**

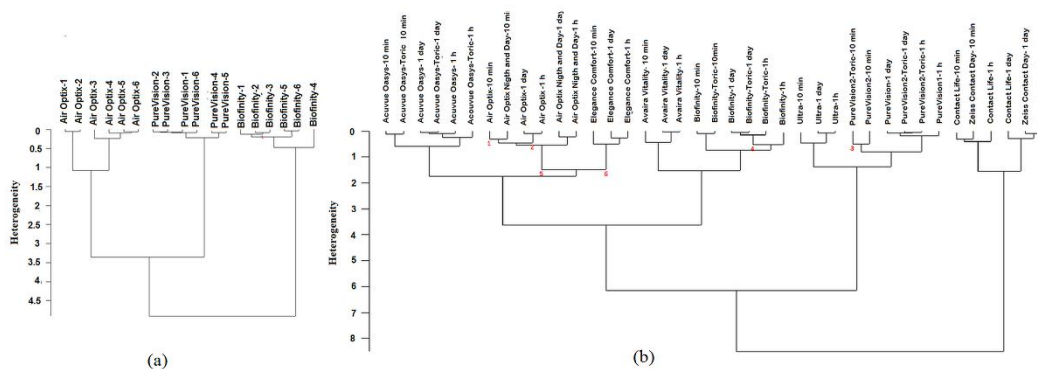
The highest and lowest water content were found in the bio-hydrogel CLs of Contact Life /Zeiss Contact brands from Wöhlk/Zeiss which are sold for sensitive and dry eyes and in SiHy CLs of Air Optic Night&Day Aqua brand from Alcon, respectively.

The second high water content are for SiHy CLs of Elegance Comfort brand from Interojo and Aveira Vitality brand from CooperVision. A close correlation was found between water content found from infrared spectra and claimed by the manufacturers (Table 1).

After 1 day, the wavenumber of the O-H stretching band shifted towards the high frequency region and the intensities of this band were decreased for all CLs. This observation shows that there is a break between the hydrogen bonds between O-H and other molecules. The intensity of the Si-O-Si stretching band in SiHy CLs *found to increase with decrease* of water content. The relationship between water content and silicon/fluorine content was examined by Dupre and Benjamin [55] and they found a negative correlation between silicon and lenses with a water content of more than 35%.

It is possible to obtain detailed information on macromolecular structures/composition from the infrared spectra. However, since the exact contents and amounts are not known in the CLs used in the study, analyses were made statistically based on the spectrum difference between the brand and copolymers.

The obtained dendrogram based on ATR-FTIR spectra of six lenses from the same box for 3 brands is represented in Fig. 5a. ATR-FTIR spectra of six lenses from the same box from each brand's lens (after 10 min, 1 h and 1 day) were averaged and subjected to HCA. The obtained dendrogram for spherical CLs of the 10 brands with PWR: -2 and toric CLs (for astigmatism) of the 3 brands is represented in Fig. 5b.

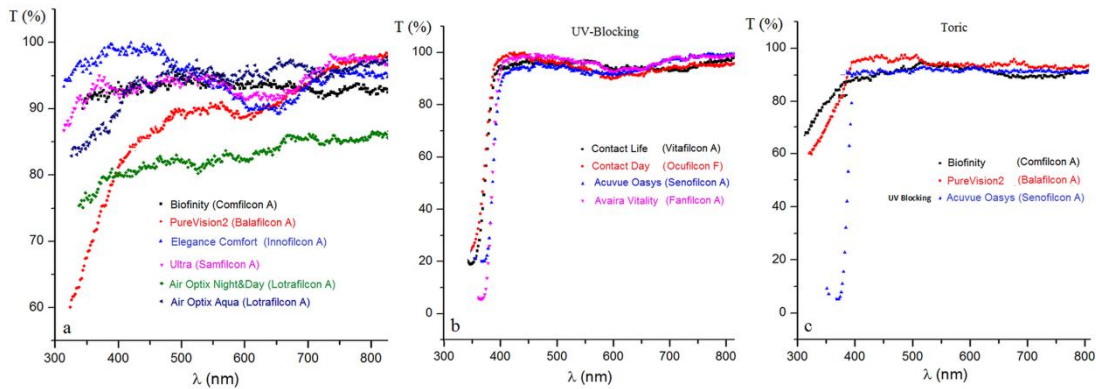


**Fig. 5. Dendrograms of Hierarchical Cluster Analysis performed with ATR-FTIR spectra of a) Three brands ( 6 lenses per box) and b) Averaged ATR-FTIR spectra of ten different brand lenses (PWR: -2, and three toric CLs ) in the 4000 – 650  $\text{cm}^{-1}$  spectral region.**

The HCA dendrograms (Figs. 5a and b) showed a good differentiation of CLs with different brands. The classification of spectra depends on molecular composition. The cluster analysis grouped all the CLs of same brand in same cluster. The high heterogeneity between bio-Hy CLs (Zeiss Contact Day/ Contact Life) and Si-Hy CLs is caused by large differences between the infrared spectra. The second high heterogeneity between Si-Hy CLs of PureVision and the other Si-Hy CLs.

### 3.1 UV-Vis Results

UV-vis transmittance spectra (315 nm - 800 nm) for spherical CLs of 6 brands (UV- blocking properties are not claim by the manufacturer), spherical CLs of 4 brands with UV- blocking (claim by the manufacturer) and toric CLs of 3 brands (claim: 1 UV-blocking and two non UV-blocking) are presented in Figs. 6 a , b and c, respectively.



**Fig 6. Percentage UVA-vis transmittance spectra as a function of wavelength of a) non UV- blocking spherical CLs b) UV-blocking spherical contact lenses c) Toric lenses**

Fig. 7a showed that different amounts of UVA were transmitted by non UV- blocking CLs of different brands. PureVision2 brand has the highest UVA protection with approximately 40% blocking among other brand, but Elegance Comfort brand has the lowest value.

Generally, the visible light transmittance of over 90% of CLs satisfied the visual requirements. Visible transmittance values between 400 nm and 800 nm of CLs of different brands except Air Optix Nigth & Day Aqua are between 90% and 98%.

Air Optix Nigth & Day Aqua brand (only for sale in Turkey, Alcon -Indonesian) has the lowest visible light transmittance (80 % -85 %). The light transmittance is found over 90 % for Air Optix (Only for sale in Turkey, Alcon- USA). Company' claim value is  $\geq 96\%$  for these brands.

Company's claim for Acuvue Oasys and Aveira Vitality of 90 % UVA protection (transmittance value 10% Claim; Class II UV-blocking). As can be seen from Fig 7b, UV-A transmittance values for CLs with UV filter of Contact Life, Zeiss Contact Day, Acuvue Oasys and Aveira Vitality brands were found between 8 % and 25 %. These transmittance values higher than the Company' claim. The different findings may due differences in the instrument and methods. These lenses could be claimed as Class II UV protectors.

Acuvue-Oasys (toric, Claim; Class I UV-blocking; block 96.1 % of UVA radiation) has the high UV-blocking properties and light transmittance (Fig 7c). Bioinfinitly (toric) and PureVision2 (toric) have low UVA blocking properties but have high visible light transmittance of over 90 % Company claim light transmittance value is  $\geq 95\%$  for these brands.

### 3.3 Refractive Indices (RI)

In general, RI of lenses are given in the range of 1.40-1.43, depending on the polymeric material and water content. Measurements are made using commercial refractometers (at approximately 590 nm light with a sodium lamp) [17,45,59].

During the measurement, the lens surface water amount affects the RI value [60]. Lens material, ECW and thickness can also alter the properties of a CL [43,61,62].

The RI values varies depending on the wavelength. In this study, the average RI values were calculated using transmittance/ reflectance spectra in the 500-600 nm and presented in Table 2 with the claimed RI values by manufacturers. Our calculated RI values show good agreement with claimed by the manufacturers except PureVision2 brand. We did not good relationship between EWC and RI values.

**Table 2 Refractive index (RI) PWR : -2 for spherical lenses**

Manufacturer	Brand name	Material (USAN)*	EWC (%)	RI	Mean RI This study
<b>Silicone hydrogel</b>					
CooperVision Hamble, UK	Biofinity	Comfilcon A 52 %	48	1.40	1.401
Bausch & Lomb Inc., Rochester, NY, USA	Pure Vision 2	Balafilcon A 64%	36	1.426	1.398
Alkon-USA Made in Malaysia <i>Only for sale in Turkey</i>	Air Optix Aqua	Lotrafilcon B 67 %	33	1.42	1.416
Alkon-USA Made in Indonesia <i>Only for sale in Turkey</i>	Airoptix Nigth &Day	Lotrafilcon A 76%	24	1.43	1.427
Interojo Inc Gyeonggi-do, Korea	Elegance Comfort	Innofilcon A 55 %	45	-	1.445
Bausch & Lomb Inc., Rochester, NY, USA	Ultra with Moisture Seal	Samfilcon A 54 %	46	1.411	1.453
Johnson & Johnson Vision Care- Ireland UV Blocking	Acuvue Oasys with Hydraclear® Plus	Senofilcon A 62%	38	1.42	1.436
Cooper Vision Scottsville, NY USA UV Blocking	Avaira Vitality	Fanfilcon A 45 %	55	1.398	1.401
<b>Bio Hydrogel</b>					
Wöhlk Contaklinsen GmbH Germany UV Blocking	Contact Life PWR :-2	Vitafilcon A 46%	54	-	1.393
Wohlk Contaklinsen GmbH Germany UV Blocking	Zeiss Contact Day PWR :-2	Ocufilecon F %45	55	-	1.398

**Table 2 (Contunie)**

<b>Manufacturer</b>	<b>Brand name</b>	<b>Material (USAN)*</b>	<b>EWC (%)</b>	<b>RI</b>	<b>Mean RI This study</b>
<b>Toric (for astigmatism) Lenses</b>					
CooperVision Hamble, UK	Biofinity	Comfilcon A 52 %	48		1.402
Bausch & Lomb Inc., Rochester, NY, USA	PureVision 2	Balafilcon A 64 %	36	1.426	1.394
Johnson & Johnson Vision Care Ireland	Acuvue Oasys	Senofilcon A 62%	38	-	1.436
UV Blocking					

### 3.4 SAXS Results

The calculated and measured scattering profiles and the obtained 3D nano- morphologies of all CLs are provided in Figure S1.

When nano-formations start to show fiber nucleation, the stacking also becomes regular and at the nanoscale, a large hump forms in the middle  $q$  ( $q$ . scattering vector size) region, which is evidence of noncrystalline structure.

Aveira Vitality, Elegance Comfort, PureVision2 (toric) and Acuvue Oasys (toric) show that similar to this type of crystalline structure. Average distance varies in the range of 7.7-17.9 nm between nanocrystalline linear lines. The UV blocking properties of these samples (except Elegance Comfort) and the addition of molecules to the polymer may be related to this linear nanostructure arrangement (Figure S1).

In the CLs of Contact-Zeiss and Contact Life, the fiber structures show parallel arrays very similar to each other at the nanoscale and resemble the structure of the real eye lens (Figure S1).

According to the manufacturer sulpho betain is the main component of Vitafilcon A hydrogel material of Contact Life brand. It was developed modelled on the good water-binding components keratan sulphate and chondroitin sulphate found in the human cornea. The material properties are very similar to those of the cornea [63].

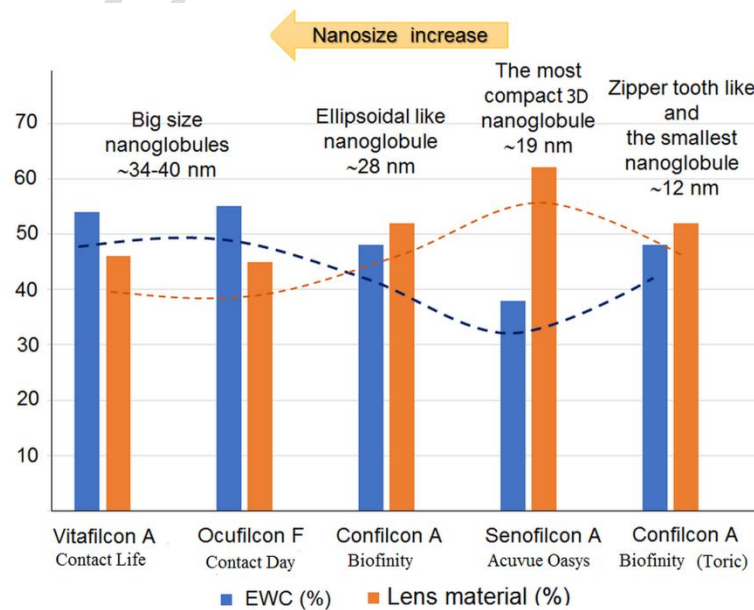
Fig. 7 depicts the most importance and evaluated results based on SAXS analyses. The nano nucleation morphologies are variable and similar to the microsize globular aggregations [64–66].

The zipper tooth like morphology and the smallest size of the nano globules (~12 nm) indicate that Bioinfinity (toric, Confilcon A) is very good nanostructured lens.

Micro size structure	Lenses with nano aggregations	Different micro-aggregations	The obtained nano-aggregations	Mean size (Radius of gyration)
Simulation of the micro-arrangement of the cells (external model)	Vitafilcon A Contact Life			$R_g = 39.9$ nm
	Ocufilecon F Contact Day			$R_g = 34.1$ nm
Simulation of the internal layers of the parallel oriented cells	Comfilcon A Biofinity			$R_g = 27.6$ nm
	Senofilcon A Acuvue Oasys			$R_g = 18.8$ nm
	Comfilcon A Biofinity (Toric)			$R_g = 11.8$ nm

Fig. 7. The correlation between simulated micro and nanoscale structures. Science photo library views were used for microscale simulations and model inspirations [63–65]

The equilibrium water content (EWC) varies depending on on the molecular, nanoscopic and microscopic structure of CLs. The volume fraction of selected polymer materials and ECW values were compared with the size of nanoglobules (Fig. 8).



## **Fig. 8. Is contact lens nanoscale structure dependent on ECW/and or lens material.**

As presented in Fig. 8, the EWC and volume fraction of polymer are effected by the size of nanoglobules of the material of CL.

## **4. CONCLUSION**

This work was designed to explain important characteristics of commercial CLs and results would have implications for future experimental and clinical research.

The effect of air drying on the water content in two groups of different brands daily wear soft contact lenses: silicone–hydrogel (lens powers -2 and -4) and bio-hydrogel by means of ATR-FTIR spectroscopy were examined in this paper. The results of ATR-FTIR seems to confirm the water content claimed by the manufacturer (not numerically in values but in order of magnitude).

The results indicate that ATR-FTIR can be successfully used to monitor the water content in soft contact lenses. It was observed that none of the lenses presented any changes depend on the lens power. There is no differences in the ATR-FTIR spectra of spherical and toric lenses of same brand.

The UV-vis transmittance/reflectance spectra of contact lenses with and without UV protection were measured. Average transmittance percentages were calculated for each lens for the UVA and vis portions of the spectrum. Comparison of the results of each lens shows that there are variable amounts of UVA absorbed and transmitted by all the contact lens brands tested. Soft contact lenses with blocking UV should be recommended.

There is not very good agreement between our reflective index (RI) values and those claimed by the manufacturers. One of the limitations of our measurement is that measure transmittance/reflectance on the lens surface and calculated RI with the assumption that the lens materials are homogenous with a uniform RI throughout the lens thickness and diameter. The second limitation: RI is sensitive to surface water contain of lens and water content can be change during measurement. Another potential limitation of our results: most of the previous studies, lens power is selected -3. A wider range of plus and minus lens powers need to be measured to confirm that there is no dependence of transmittance/reflectance/ RI on lens power and correlated center thickness changes.

Nanoscale formations and nucleations aggregate the core of microscale structures. For this reason, nanomorphologies plays a fundamental role in micro-formations and bigger size aggregations. Size and shapes of the nanoglobules are effective on lens parameters.

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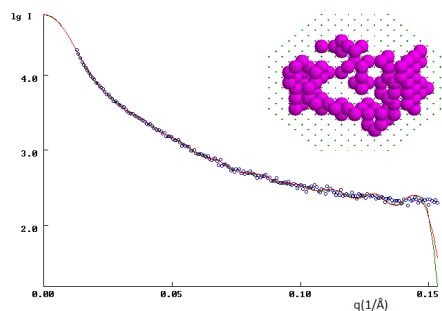
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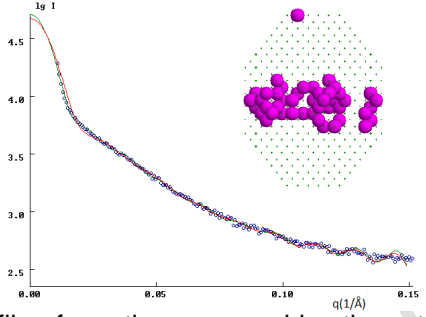
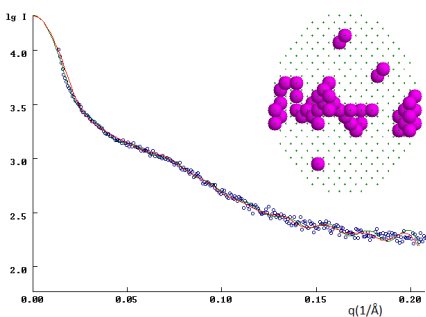
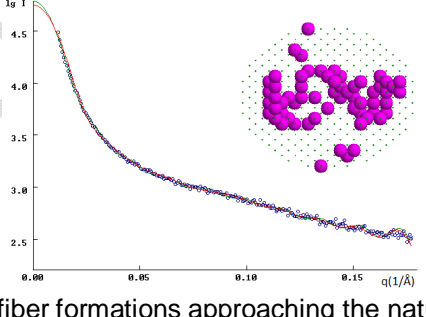
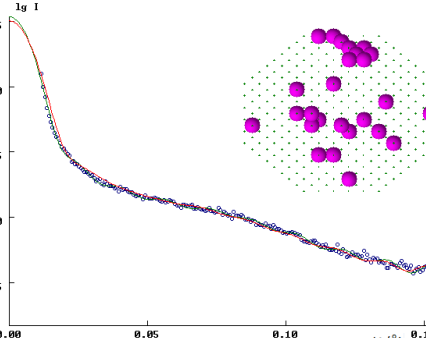
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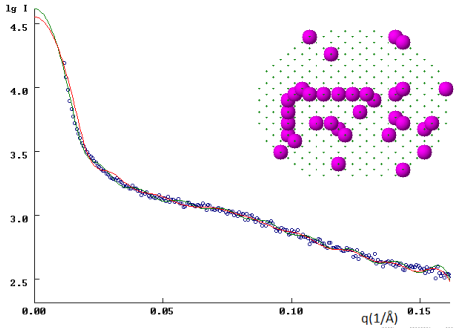
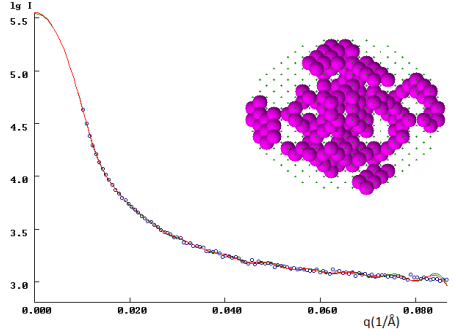
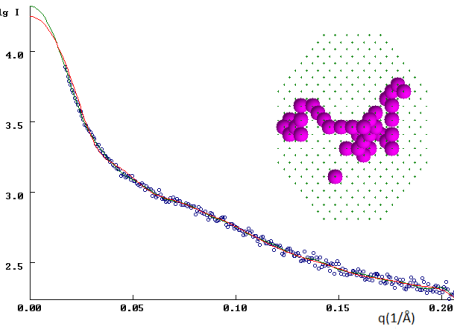
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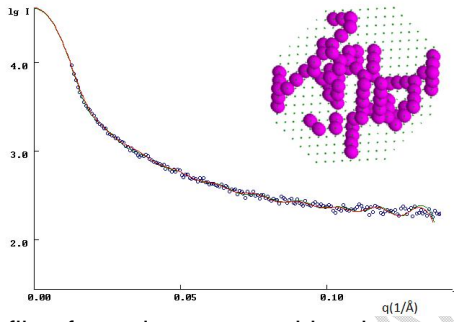
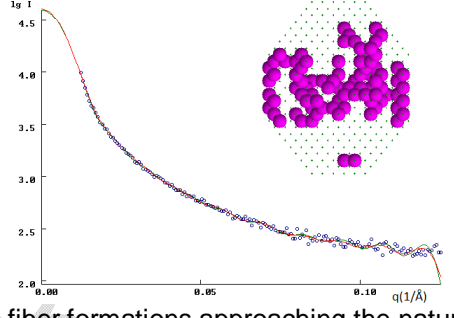
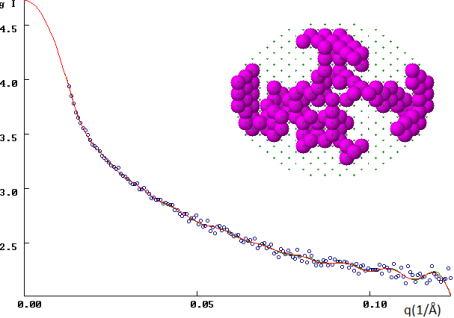
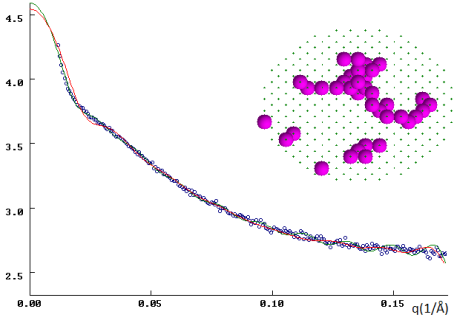
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**Supplementary Figure/Table**

<b>Figure S1</b> SAXS patterns of studied soft contact lenses and the obtained 3D morphologies of the nanoparticles.		
<b>Manufacturer/Brand</b>	<b>Material</b>	<b>log I-q graphs</b>
CooperVision Hamble, UK  Biofinity	Comfilcon A	 <p>The most suitable nano-scale nucleation for natural lens structure</p>

<p>Bausch &amp; Lomb Inc., Rochester, NY,USA</p> <p>Pure Vision 2</p>	<p>Balafilcon A</p>	 <p>Clusters of fiber formations approaching the natural lens structure</p>
<p>Interojo Inc.Kore</p> <p>Elegance Comfort</p>	<p>Innofilcon A</p>	 <p>Formations show clustering. <math>d = 9.4 \pm 0.3</math> nm</p>
<p>Bausch &amp; Lomb Inc., Rochester, NY,USA</p> <p>Ultra Moisture Seal</p>	<p>Samfilcon A</p>	 <p>Clusters of fiber formations approaching the natural lens structure</p>
<p><b>Figure S1 (Continue) Manufacturer/Brand</b></p>	<p><b>Material</b></p>	<p><b>log I-q graphs</b></p>
<p>Alkon, Endonezya</p> <p><b>(for Turkey)</b></p> <p>Air Optix Nigth &amp; Day Smartshield techn.</p>	<p>Lotrafilcon A</p>	

<p>Alkon, Endonezya</p> <p><b>For Turkey</b></p> <p>Air Optix Aqua</p> <p>Smartshield techn</p>	<p>Lotrafilcon A</p>	<p>Random structure without any nanoformation</p>  <p>Irregular structure containing fiber structure start</p>
<p>Johnson &amp; Johnson Vision care Jacsonville USA</p> <p><i>Acuvue Oasys with hydraclear plus</i></p> <p>UV Blocking</p>	<p>Senofilcon A</p>	 <p>Nanonucleation most suitable for natural lens structure at micro scale</p>
<p><b>Figure S1 (Continue)</b></p> <p><b>Manufacturer/Brand</b></p>	<p><b>Material</b></p>	<p><b>log I-q graphs</b></p>
<p>Cooper Vision USA Avaira Vitality</p> <p>UV Blocking</p>	<p>Fanfilcon A</p>	 <p>Formations show clustering. <math>d= 9.0\pm 0.4</math> nm</p>

<p>Wöhlk Kontaktlinsen GmbH Germany</p> <p>Contact Life</p> <p>UV Blocking</p>	<p>Vitafilcon A</p>	 <p>Clusters of fiber formations approaching the natural lens structure</p>
<p>Wohlk Kontaktlinsen GmbH Germany</p> <p>Zeiss Contact</p> <p>UV Blocking</p>	<p>Ocufilecon F</p>	 <p>Clusters of fiber formations approaching the natural lens structure</p>
<p>CooperVision Hamble, UK</p> <p>Biofinity</p>	<p>Comfilcon A</p> <p><b>Toric</b></p>	 <p>Nanonucleation most suitable for natural lens structure at micro scale</p>
<p>Bausch &amp; Lomb Inc., Rochester, NY, USA</p> <p>Pure Vision® 2</p>	<p>Balafilcon A</p> <p><b>Toric</b></p>	 <p>Formations show clustering. <math>d = 17.9 \pm 0.5</math> nm</p>

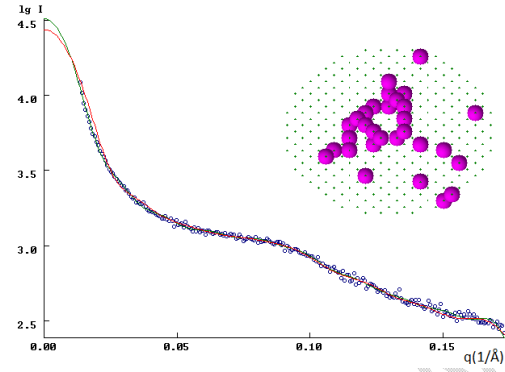
Johnson & Johnson  
Vision care  
Jacksonville USA

Acuvue  
Oasys with  
HYDRACLEAR® PL  
US

UV Blocking

Senofilcon A

**Toric**



Formations show clustering  $d = 7.7 \pm 0.3$  nm

UNDER PEER REVIEW