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OPTICAL AND SURFACE PROPERTIES OF ACRYLIC COPOLYMERS FOR CRYSTALLINE LENS IMPLANTS

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The paper presents experimental results concerning optical and surface properties of a series of acrylic copolymers obtained by free-radical mass copolymerization. This study is part of a research project on polymeric biomaterials with potential use for new crystalline lens implants which could restore visual accommodation. The following monomers were used to obtain acrylic copolymers: metyl metacrylate, cyclohexyl metacrylate, 2ethyl hexyl acrylate, butyl acrylate. The wettability of these copolymers was investigated through measurements of static contact angle with water. Their refractive indices were determined by UV-visible spectroscopic ellipsometry.

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1. Introduction

When cataract surgery is performed the opaque content within the capsule of the lens is extracted and an intraocular lens made out of synthetic polymeric biomaterials is implanted in its place [1]. An ophtalmological microscope for surgery has been developed and reported in [2]. After cataract surgery, visual accommodation through the biologic mechanism is lost [3]. A way to recover visual accommodation is to design an implant with mechanical and optical properties close to those of the crystalline lens content [4, 5]. The work presented in this paper is part of a study which aims at assessing the potential that hydrophobic acrylic copolymers have as polymeric material for such an implant. Our research interests in hydrophobic acrylic copolymers are related to clinical studies results. With regards to long term biocompatibility for intraocular lens use, these copolymers perform better in comparison with other types of polymers (acrylic hydrogels, silicones) [3]. Several acrylic copolymers were obtained by free radical mass copolymerization and their optical, mechanical and surface properties studied. This article presents the way the optical and surface properties were investigated and discussed.

2. Materials and sample preparation

The following acrylic monomers were used to obtain copolymers, purchased from Aldrich and Fluka: methyl methacrylate (MMA), cyclohexyl methacrylate (CHMA), 2ethyl hexyl acrylate (EHA), butyl acrylate (AB), and ethylen glycol dimethacrylate (EGDM). Pairs of comonomers consisted of a methacrylate and an acrylate, in 5 molar ratios for a given pair: 40/60, 45/55, 50/50, 55/45, and 60/40. There were four series of copolymers obtained: MMA/AB, MMA/EHA, MMA/EHA with 1wt% EGDM and CHMA/EHA. AIBN was used as initiator, 0.2wt% based on the total amount of comonomers. The copolymerization was carried out for 14h at 60 ºC, followed by 1h

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at 65 ºC, 1h at 70 ºC, 1h at 75 ºC, 1h at 90 ºC. The moulds used consisted of two square plates, one of glass and one of aluminium, separated by a polyvinyl chloride wire to give polymeric samples of 1 mm width.

3. UV-visible spectroscopic ellipsometric measurements

Ellipsometric measurements were carried out with a SOPRA GESP5 rotating polarizer instrument. Measurements were done at 589 nm, with an incidence angle between 45 and 65 degrees, in 0.5 degrees steps. The optical modelling of the ellipsometry data was carried out using the Winelli 4.09 software (Sopra, Bois Colombes, France). Optical properties were described by a Cauchy dispersion law for *n* and *k*. The adjustment of the parameters was done using the Levensberg-Marquadt algorithm over the tanΨ and cosΔ functions.

4. Contact angle measurements

Measurements of static contact angle were performed by capturing the image of the profile of water drop on the surface. An experimental set-up consisting of a high-resolution black and white camera mounted on a microscope connected to a PC was used. The image was then processed with an edge detection algorithm and the profile of the drop was found. The Young-Laplace equation together with the boundary conditions provided by the static contact angle, position and knowledge of the total volume describes the shape of free surfaces for liquids in static equilibrium. Its solution was fitted to the experimental profile to determine the static contact angle.

5. Results and discussion

Refractive index

The values of the refractive indices of the polymeric samples (Table 1) were found to be between the refractive indices of literature reported values for the respective homopolymers: poly(methyl methacrylate) - 1.49, poly(cyclohexyl methacrylate) – 1.50, poly(n-butyl acrylate) – 1.47. No significant differences were found for compositions of same co-monomers and different molar ratios. For two samples of 60% acrylate molar content of the monomers composition it was not possible to make a correct measurement. There were problems with the alignment due to the lack of planarity of these samples, which are elastomers from the point of view of mechanical behaviour.

Table 1. Refractive indexes of the copolymers obtained.

Molar ratio →	40/60	45/55	50/50	55/45	60/40
Co-monomers					
MMA/AB	1.472	1.472	1.48	1.476	1.484
MMA/EHA	-	1.482	1.482	1.478	1.477
MMA/EHA/1%EGDM	1.480	1.482	1.488	1.485	1.485
CHMA/EHA	-	1.481	1.476	1.481	1.487

Wettability

For each surface, at least 6 measurements of static contact angle with water were taken. The values found were between 80º and 100º. This proves that the surfaces of the copolymers are hydrophobic, as expected.

For each surface, a range of values for the contact angle was found. Differences in measurement results for the same surface were found up to 18 degrees. The median values of the range of contact angle values for each surface are presented in Table 2. The difference between the highest and the lowest value measured for each surface is presented in Table 3.

Table 2. Static contact angle – median values of the range of contact angle values.

Molar ratio → / Co-monomers	40/60	45/55	50/50	55/45	60/40
MMA/AB	89	89.5	90	88.5	88
MMA/EHA	91	92	92	91	91
MMA/EHA/1%EGDM	92	91.5	94	92	96
CHMA/EHA	96	90	90.5	94	98

The data obtained presented in Table 2 does not show any clear tendency in contact angle median values related to changes in composition, given that the overall error for our contact angle measurement experimental set-up is +-3º. The differences in chemical structure of the comonomers used do not change the overall hydrophobicity of the surfaces.

The existence of a range of contact angle values is related to the surface roughness and its chemical heterogeneity [5]. Thus, the data presented in Table 3 give information regarding the hysterisis of the contact angle. The copolymers which are richer in methacrylate have thermoplastic behaviour, are rigid and have increased roughness in comparison with those with more acrylate content, which are elastomers. This would explain a wider range of contact angle values for thermoplastic copolymers.

Table 3. The difference between the highest and the lowest contact angle values measured for each surface.

Molar ratio → / Comonomers	40/60	45/55	50/50	55/45	60/40
MMA/AB	6	4	10.5	6	18
MMA/EHA	3,5	7.5	5.5	12	7
CHMA/EHA/1%EGDM	2.5	3	3	2	1.5
CHMA/EHA	16	3	8	4.5	10.5

Still, there are compositions with 60 percent acrylate (CHMA/EHA 40/60) which show a wide range of values as well. This could be related mainly to surface chemistry heterogeneity, caused by mass copolymerization in accordance with molar ratios and reactivity ratios of the comonomers. In the case of the MMA/EHA with 1wt% EGDM compositions, the range of contact angle values is considerably narrowed. This shows the reticulation agent to give smoother and more homogenous surfaces.

6. Conclusions

The acrylic co-polymers obtained by free radical mass copolymerization have a particular hysterisis of the contact angle, related to the surface chemistry heterogeneity. While changes of molar ratios of the comonomers and differences in their chemical structure clearly affected the

mechanical properties of the copolymers obtained, they did not change the overall surface hydrophobicity. The differences between the refractive indices of the polymeric samples are low.

The experimental results obtained with this type of copolymer give reason to consider it suitable for a composite implant similar to the discrete nature of the mechanical and optical properties of the biological lens. Further work is envisaged to asses the possibility of designing such an implant and its potential for rehabilitating accommodation.

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