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Research article

Towards improving the biocompatibility of prosthetic eyes

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ABSTRACT

Prosthetic eyes are currently manufactured using Poly(methyl methacrylate) (PMMA) which is not an ideal material because it is hydrophobic. While significant research has investigated the benefits of hydrophilic materials for contact lenses, no such research has been carried out on hydrophilic materials for prosthetic eyes until now. In this study, different derivatives of Poly(ethylene glycol) (PEG) monomer and methyl methacrylate (MMA) monomer were grafted to PMMA using copolymerisation. The resulting matrixes were evaluated by water contact angle measurement, 24 h water absorption testing, and colour-difference measurement when exposed to ultraviolet light. The contact angle and water absorption results indicated that ethylene glycol dimethacrylate (EGDMA) grafted PMMA matrix had a better hydrophilic performance than the other matrixes tested. EGDMA is already a minor constituent of the PMMA matrix currently used for manufacturing prosthetic eyes but when the proportion of EGDMA monomer to MMA monomer used in the manufacturing process was increased to 50/50 the hydrophilicity of the matrix was significantly improved.

EGDMA-grafted PMMA is inexpensive and comes as a liquid monomer that is easily mixed with the PMMA monomer that ocular prosthetists are familiar with. The mixture requires no special handling beyond the normal safety precautions that apply when using PMMA monomers. In-vitro testing shows that EGDMA-grafted PMMA significantly improves the wettability of PMMA currently used for the manufacture of prosthetic eyes and has the potential to significantly improve wearing comfort and socket health.

1. Introduction

1.1. Description of prosthetic eyes and prosthetic eye materials

When an eye is lost for any reason, e.g from congenital causes, diseases or accidents, it is usually replaced with a prosthetic eye. This is a device that fits under the eyelids and within the anophthalmic socket and is designed to restore appearance, facial symmetry and eyelid function.

The anterior surface of a prosthetic eye is analogous to a the anterior surface of a contact lens but while significant research has investigated the benefits of hydrophilic materials for contact lenses [1, 2, 3, 4] no such research has been carried out on hydrophilic materials for prosthetic eyes.

Tear protein deposits accumulate during use on both the anterior and posteror surfaces of prosthetic eyes. The anterior surface of the prosthesis has two zones, the interpalpebral zone (between the upper and lower lids) and the retro-palpebral zone (the parts of the anterior surface that are always covered by the lids). These deposits make these surfaces more hydrophilic (more wettable) and this has been shown to be associated with sockets having less conjunctival inflammation and less mucoid discharge [5]. However, the interpalpebral anterior surface of a prosthetic eye is subject to the wiping action of the eyelids during blinking and helpful deposits do not accumulate in this area [6] (See Figure 1). Because there are no accumulated deposits the lubricity of this central anterior part of the prosthesis is determined by the hydrophilicity of the raw unmediated surface of the prosthesis material.

Except for glass eyes which are made in several European countries [7], prosthetic eyes are made from poly(methyl methacrylate) (PMMA). The PMMA matrix is polymerized by the reaction of acrylic powder with liquid monomer. The powder consists of a mix of PMMA polymer, methyl methacrylate (MMA) monomer, and dibenzoyl peroxide (BPO). The liquid is a blend containing methyl methacrylate (MMA) monomer and ethylene glycol dimethacrylate (EGDMA) monomer. The BPO in the acrylic powder is capable of initiating the polymerization of monomers

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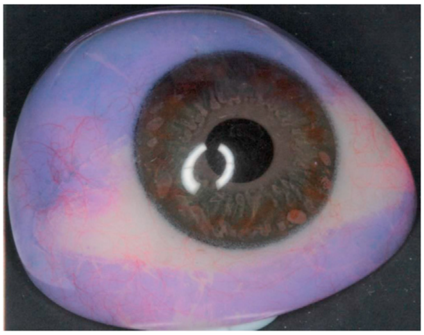

Figure 1. Stained tear protein deposits (blue-purple) occupy the retro-palpebral zone of the anterior surface of this prosthetic eye while the wiping action of the eyelids keeps the inter-palpebral zone clear.

and is included in the existing polymer. A typical heat curing acrylic based on MMA is Vertex™ Rapid Simplified [8]. It is primarily used for the manufacture of dentures but is also commonly used for the manufacture of prosthetic eyes. Its composition is listed in Table 1.

Table 1. The composition of acrylic powder and liquid monomer found in the material Technical Data Sheet on "Vertex™ Rapid Simplified" [7].

	Ingredients	%	Description
Acrylic powder	PMMA	>95	Polymer
	MMA	<1	Monomer
	BPO	<1	Initiator
Liquid monomer	MMA	>95	Monomer
	EGDMA	<5	Cross-linking agent

MMA = Methyl methacrylate, PMMA = Poly (Methyl methacrylate), BPO = Dibenzoyl peroxide, EGDMA = Ethylene glycol dimethacrylate.

1.2. Potential discomfort from hydrophobic PMMA prosthetic eyes

PMMA polymer is an effective material for manufacturing ocular prostheses because of its excellent light transmission, resistance to biodegradation, resistance to fluid diffusion, excellent optical clarity, together with ease in processing, polishing and modifying [9]. However, PMMA is relatively hydrophobic and this property is a potential cause of discomfort to the wearer. Not only does the hydrophobic nature of PMMA increase the likelihood of tear protein deposits and other debris settling on the interpalpebral anterior surface of the prosthesis but the low wettability will discourage the formation of a stable tear film. See Figures 2 and 3. The poor wettability of a PMMA surface may contribute to a number of anophthalmic socket disorders such as dryness, meibomian gland dysfunction, lacrimal drainage blockage, excessive mucoid discharge and lagophthalmos [10, 11].

1.3. Hydrophilic monomers

Hydrophilic monomers such as 2-hydroxyethyl methacrylate (HEMA), hydroxyalkyl methacrylates (HAA), N-vinylpyrrolidinone (NVP), N,N-dimethyl acrylamide (DMA) have been used in contact lenses [12]. The improvement of the HEMA polymer formulations through addition of various hydrophilic monomers increased the water content and enhanced the permeation of oxygen, however HEMA-based hydrogels can only be worn for less than 6 days [13]. NVP is a common hydrophilic monomer which is frequently used to increase the water content of the contact lens material, however NVP can also enhance the relative evaporation rate of water, which gives rise to a rough surface on the soft contact lens [14].

1.4. Hydrophilic polymers

A promising approach to improve the hydrophilicity (wettability) of PMMA is to introduce hydrophilic polymers into its formulation. Polyethylene glycol (PEG) and its derivatives are generally known as hydrophilic polymers [4]. The PEG and its derivatives are composed of hydrophilic polyether compounds with repeating ethylene glycol units which are highly soluble in water [15]. Moreover, PEG has been proved to be both non-toxic and non-immunogenic, which are essential requirements for biomaterials [16]. PEG and various PEG compounds are approved by the United States food and drug administration (FDA) for human use and have been widely used in biological research and industry [17].

Previous studies have also suggested that PEG and its derivatives are relatively safe for use in the medical field under the present conditions of intended use [18]. For example, PEGs are used as gene carriers or drug vehicles. Kim et al. introduced the PEG that created a tree-like triblock copolymer for use in gene delivery systems. The novel triblock co-polymer Polyamidoamine (PAMAM) - PEG-PAMAM copolymer was synthesised and applied as a gene carrier. This copolymer was found to form highly water-soluble polyplexes with plasmid DNA and showed little cytotoxicity [19]. Choi et al. studied the biological reagents derived from luminescent rhenium (I) polypyridine complexes modified with a polyethylene glycol (PEG). They found that the PEG-grafted complexes showed significantly higher water solubility and lower cytotoxicity than their PEG-free counterparts [20]. Hence, PEG and its derivatives are likely to be desirable polymers for increasing the hydrophilicity of PMMA prosthetic eyes. The small quantity of EGDMA (one of the derivatives of PEG) that is already present in Vertex™ Rapid Simplified material is insufficient to produce a level of hydrophilicity expected to benefit wearers of prosthetic eyes.

1.5. Grafting hydrophilic polymers to PMMA

One common strategy to introduce PEG and its derivatives to PMMA is grafting through copolymerisation of MMA with PEG macromonomer

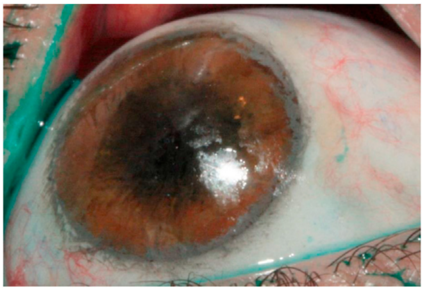

Figure 2. Lissamine green stain highlights tear protein deposits on the interpalpebral surface of a PMMA prosthetic eye. These aggregations are usually swept away by blinking but irritate the eyelids if they dry out.

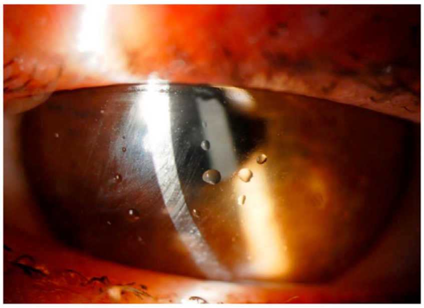

Figure 3. Slit lamp biomicroscope view showing the result of tear-film break-up on the surface of a PMMA prosthetic eye. Published with kind permission of Sloan Medical Ltd. All rights reserved.

(macromonomer method). Among all the grafting copolymerisation methods, the *graft through copolymerisation* method is one of the simplest ways to synthesise graft copolymers with desirable side chains [21]. The mechanism of copolymerisation of MMA monomer and PEG macromonomer is described in Figure 4 [22]. The MMA monomer is radically copolymerised with a methacrylate functionalised PEG macromonomer. This method permits incorporation of hydrophilic PEG macromonomers into the PMMA backbone. Extensive research on the use of copolymerisation to graft PEG branches into the PMMA backbone has shown that the hydrophilicity of the copolymer can be adjusted by adapting the feed ratio of MMA monomer and PEG macromonomer. For example Bouhier et al. [23] synthesised a branched PMMA with a PEG hydrophilic branch by copolymerisation of MMA and ethylene glycol dimethacrylate (EGDMA) monomers using atom transfer radical polymerization (ATRP). The structure of the copolymer was adjusted by changing the feed ratio of MMA and EDGMA. High yields of branched PMMAs can be obtained without crosslinking by appropriate adjustment of the molar feed of MMA/EGDMA/initiator. Rosa et al. [24] prepared a branched copolymer (PMMA-co- poly (ethylene glycol) methyl ether methacrylate (PEGMA)) with PEG as a hydrophilic branch and PMMA as a hydrophobic backbone by copolymerisation of PEGMA and MMA using ATRP. The hydrophilicity of the resulting copolymers was altered by adjusting the molar ratio of MMA and PEGMA. It was also shown that the solubility of the copolymer increased with the increasing of PEGMA content.

1.6. Aims of the study

This study aimed to improve the biocompatibility of prosthetic eyes by improving the surface hydrophilicity of the PMMA material currently used in their manufacture by:

(a) grafting different PEG derivatives to PMMA and a preliminary investigation of their physical properties with respect to surface hydrophilicity, water absorption and ultraviolet light (UV) resistance;
(b) selecting the most promising copolymerised PEG derivative (EGDMA) and performing a detailed investigation of surface hydrophilicity and ultraviolet light (UV) resistance;
(c) testing different blends of EGDMA/MMA mix to determine which ratio provides the most hydrophilic PMMA surface and;
(d) investigating the effect of different polishing grades on the surface of the most hydrophilic material found.

The results will inform subsequent investigations into the response of the anophthalmic socket to this new class of material.

2. Methods

2.1. Properties of different PEG derivatives

Vertex™ Rapid Simplified acrylic and three different PEG grafted PMMA polymer sheets (PEGMEA, PEGMEMA, and EGDMA grafted sheets) were selected for this study. Their physical properties were explored by measuring hydrophilicity, UV resistance and water absorption. The chemicals and materials used are listed in Table 2.

2.1.1. Preparation of samples of different PEG derivatives

Six polymer samples were synthesised using a number of different PEG derivatives grafted to a PMMA matrix through copolymerisation. The synthesis procedure for each sample was as follows: Liquid monomer (1ml) and acrylic powder (2.3g) were put into a 50 ml beaker. The mixture was stirred with a glass rod for 30 s and left at room temperature (generally taken as about 20 °C) for 15 min before it was kneaded into a flat sheet. The sheet was then heated to 100 °C and held at this temperature for 20 min.

The detailed ingredients of the resulting samples are listed in Table 3.

Sample 1 was a pure PMMA sheet.

Sample 2 was the control PMMA sheet which was provided by Vertex Dental.

Sample 3 was a PMMA grafted with 3.35 wt.% of PEGMEA.

Sample 4 was a PMMA grafted with 3.35 wt.% of PEGMEMA.

Sample 5 was a PMMA grafted with 1.62 wt.% of EGDMA.

Sample 6 was a PMMA grafted with 4.89 wt.% of EGDMA.

2.1.2. Hydrophilicity measurement

A goniometer was used to measure the water contact angles of the samples in accordance with ASTM D7334 – 08 (Standard Practice for Surface Wettability of Coatings, Substrates and Pigments by Advancing Contact Angle Measurement) [25]. All samples were cleaned by an ultrasonic cleaner in 97% ethanol to remove contaminants and allowed to dry before measurement. The contact angles were measured using distilled water dropped onto the samples. A 20 s interval separated initial and static contact angle measurements and the final wetting angle was calculated as the mean of the left and right contact angles of the water droplet.

2.1.3. Water absorption measurement

The percentage increase in weight of the samples during 24 h of water immersion was measured in accordance with ASTM D570 – 98 (Standard Test Method for Water Absorption of Plastics) [26].

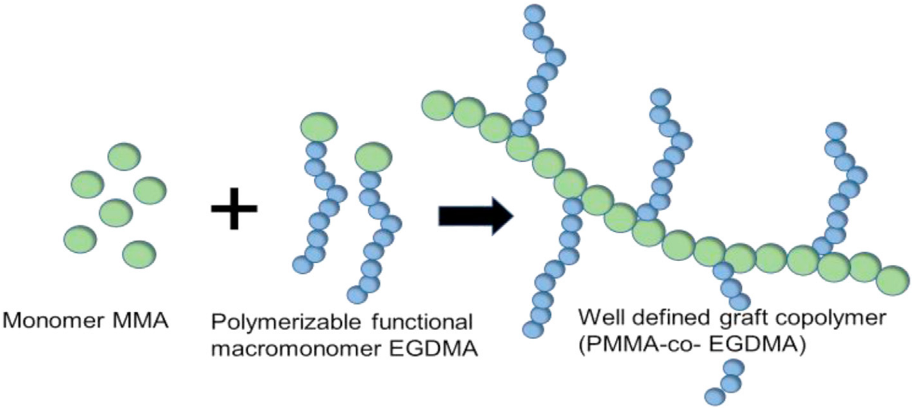

Figure 4. The mechanism of copolymerisation of MMA and PEG macromonomer [18].

Table 2. Chemicals and materials used in the modifications of PMMA.

Name	Abbreviation	Description by the supplier
Acrylic powder	-	Vertex Dental: PMMA, MMA, BPO
Liquid monomer	-	Vertex Dental: MMA, EGDMA (<5%)
Methyl methacrylate	MMA	Sigma-Aldrich: contains ≤30 ppm monomethyl ether hydroquinone (MEHQ) as an inhibitor
Ethylene glycol dimethacrylate	EGDMA	Sigma-Aldrich: contains 90–110 ppm MEHQ as an inhibitor
Poly (ethylene glycol) methyl ether acrylate	PEGMEA	Sigma-Aldrich: Mn~480, contains 100 ppm BHT as an inhibitor, 100 ppm MEHQ as an inhibitor
Poly (ethylene glycol) methyl ether methacrylate	PEGMEMA	Sigma-Aldrich: Mn~300, contains 100 ppm MEHQ as an inhibitor, 300 ppm BHT as an inhibitor
Ethanol	EtOH	Wax cleaner

2.1.4. *UV resistance measurement*

Accelerated weathering that simulates the damaging effects of long-term outdoor exposure of polymers was measured in accordance with ASTM D4329 – 13 (Standard Practice for Fluorescent Ultraviolet (UV) Lamp Apparatus Exposure of Plastics) [27]. This was done using QUV testing. QUV testing was performed with a QUV accelerated weathering tester (Q-Lab Corporation, Wavelength: 340 nm, 100 h exposure [28]. The colour change after UV exposure was detected by a Minolta CR-200B Handheld Chroma Meter in accordance with ASTM E1347 – 06 (Standard Test Method for Color and Color-Difference Measurement by Tristimulus Colorimetry)) [29].

The colour change of samples during QUV testing was described by the CIE Lab method, which determines the lightness (L), redness (a) and yellowness (b). The total colour difference (ΔE) was calculated using Eq. (1).

$$\Delta E = [\Delta L^2 + \Delta a^2 + \Delta b^2]^{1/2} \tag{1}$$

Where ΔL, Δa, and Δb represent the differences between the initial and final values of L, a, and b, respectively. A positive ΔL stands for lightening, and a negative ΔL stands for darkening. A positive Δa indicates a colour shift toward red, and a negative Δa indicates a colour shift toward green. A positive Δb signifies a shift toward yellow, and a negative Δb signifies a shift toward blue.

2.2. *Properties of EGDMA grafted material*

2.2.1. *Preparation of samples of EGDMA grafted material*

For this next experiment, eight samples were synthesised by adding 1.00ml of Vertex™ MMA monomer grafted with different ratios of EGDMA to Vertex™ heat cure clear PMMA acrylic powder. After 15 min during which time the materials were blended to homogeneity, the resultant dough was kneaded and placed in a mould. The material was polymerised by placing the pressurised mould in water which was brought to the boil over a 30-minute period and held at 100 °C for 20 min. The surface was finished using dental laboratory pumice applied with a wet calico polishing mop and then a polishing compound for dental plastics final polish (Bego, Lincoln, RI, USA) [30] which was applied with a dry calico polishing mop. The Bego product is no longer in production but is similar to other commercially available denture polishing compounds. The ratios of liquid EGDMA monomer mixed with liquid Vertex™ MMA monomer in the samples are listed in Table 4.

Table 3. The ingredients used to create the six resultant polymer samples.

Sample number	Volume of Monomer (mls)					Weight of Clear acrylic powder (gms)
	Vertex™	MMA	PEGMEA	PEGMEMA	EGDMA	
1		1.0				2.3
2 (control)	1.00					2.3
3	0.90		0.1			2.3
4	0.90			0.1		2.3
5	0.95				0.05	2.3
6	0.85				0.15	2.3

Vertex™ = Vertex™ Rapid Simplified Poly(methyl methacrylate). MMA = Methyl methacrylate. PEGMA = Poly(ethylene glycol) methyl ether methacrylate. PEGMEMA = Poly (ethylene glycol) methyl ether methacrylate. EGDMA = Ethylene glycol dimethacrylate.

2.2.2. *Polishing grade measurement*

Three further samples of prosthetic eye material were created with 50% EGDMA (0.5ml) grafted to Vertex™ MMA monomer (0.5ml) in 5 gms of Vertex™ acrylic powder. Sample one was polished with dental laboratory pumice applied with a wet calico mop (Low polish). Sample two was prepared as for sample one before a commercially available denture polishing compound was applied with a dry calico mop (Medium polish). Sample 3 was prepared as for samples 1 & 2 before being polished with aluminium oxide paste applied with a rotating foam polyurethane disc to achieve an optical quality contact lens polish grade (High polish).

3. Results

3.1. *Properties of different PEG derivatives*

The properties of resulting polymers are listed in Table 5.

3.1.1. *Hydrophilicity*

The polymerized material with MMA and control Vertex™ monomers (samples 1 & 2) had water contact angles of 87.8° and 81.9° respectively. Samples 3, 4 and 6 had lower water contact angles indicating that the PEG grafted onto the PMMA matrix increased the wettability of the samples.

Of the PEG derivatives, the EGDMA-grafted PMMA (0.15ml) sample produced the lowest contact angle. The EGDMA-grafted PMMA (0.05ml) sample produced a water contact angle very similar to the control PMMA sample (sample 2), which is to be expected as the Control Vertex™ formulation contains a small amount of EGDMA (<5%). It appears that

Table 4. The volumes of EGDMA mixed with Vertex™ monomer in the eight samples.

Sample Number	Volume of Vertex™ MMA liquid monomer (ml)	Volume of EGDMA liquid monomer (ml)	Weight of Vertex™ acrylic powder (gms)
Control	1.0	0	5
1	0.9	0.1	5
2	0.8	0.2	5
3	0.7	0.3	5
4	0.6	0.4	5
5	0.5	0.5	5
6	0.4	0.6	5
7	0.3	0.7	5
8	0.2	0.8	5

Vertex™ = Vertex™ Rapid Simplified methyl methacrylate monomer and poly(methyl methacrylate) acrylic powder. MMA = Methyl methacrylate. EGDMA = Ethylene glycol dimethacrylate.

Table 5. The properties of the resultant polymers.

Samples	Contact angle (°)	Water absorption (%)	Colour change after QUV(Δ E)
1 PMMA	87.7	39.72	2.96
2 Control Vertex™	81.9	48.26	8.72
3 PEGMEA	69.9	52.48	9.28
4 PEGMEMA	75.3	31.64	11.63
5 EGDMA (0.05ml)	81.5	59.66	8.17
6 EGDMA (0.15ml)	60.3	39.48	7.48

EGDMA present in amounts under 15% is not sufficient to lower the water contact angle.

Given these initial results, EGDMA grafting was selected to investigate further.

3.1.2. *Water absorption*

Table 5 shows the percentage of water absorbed for each of the polymer samples. The PEG derivatives grafted onto PMMA (including EGDMA already present in Vertex™ monomer - sample 2) showed higher water absorption than the pure MMA/PMMA matrix (sample 1).

The EGDMA-grafted PMMA samples showed higher water absorption than the other two PEG derivatives. For EGDMA-grafted PMMA, the water absorption increased as the amount of EGDMA in the samples increased.

3.1.3. *UV resistance*

Table 6 and Figure 5 show the colour change after QUV testing for all polymer samples. All samples' Δb were positive after 100 h UV exposure, indicating that the yellowing occurred during exposure. All the PEG derivatives grafted PMMA had higher colour difference (ΔE) values compared to pure PMMA (sample 1). The colour difference (ΔE) value of EGDMA-grafted PMMA was lower than for the other PEG groups. For EGDMA-grafted PMMAs, there appeared to be no correlation between the amount of EGDMA and colour difference. No signs of degradation or deterioration of the surfaces were observed after QUV testing.

3.2. *Properties of EGDMA grafted material*

The water contact angle and water absorption of polymerised Vertex™ acrylic containing different ratios of EGDMA are shown in Figures 6 and 7. The data in the figures are left and right contact angle averages of 3 replicates.

The results indicated that the EGDMA monomer had been successfully grafted to the PMMA matrix and that the wettability of PMMA was increased after grafting EGDMA. The addition of EGDMA up to 40% by volume caused a significant decrease in contact angle but the effect leveled off and the difference between 40% and 80% was less notable, although 80% EGDMA still exhibited the lowest contact angle.

The low percentages of water absorption were negatively correlated with the contact angle results.

3.2.1. *Polishing grades for 50% EGDMA grafted prosthetic eye material*

The contact angles for three polish grades applied to 50% EGDMA grafted to Vertex™ PMMA was highest for the low polish grade, and lowest for the medium grade. The data in Figure 8 are averages of 3 replicates. The contact angles for all three polish grades negatively corresponded with their water absorption percentages (Figure 8).

4. Discussion

The hydrophilic polymer, poly (ethylene glycol) and its derivatives are generally known to improve the hydrophilicity of PMMA [4] but in order to find the derivation best suited to prosthetic eyes it was necessary to compare three different PEG grafted PMMA polymer sheets (PEGMEA, PEGMEMA, and EGDMA grafted sheets) with each other, with pure MMA and with a control PMMA. These tests were designed to rule out possible negative characteristics from water absorption and colour instability as well as to compare the hydrophilic properties of the various PEG derivatives. This part of the investigation was precautionary rather than exploratory and as such only one sample of each PEG derivative was used.

The EGDMA-grafted PMMA matrix had better hydrophilic performance and water absorption properties for prosthetic eyes than the other matrixes and the hydrophilicity of the matrix increased with the

Table 6. Colour change in samples after 100 h of exposure to UV lamps of wavelength 340 nm in the QUV machine.

Sample	Colour before UV exposure		Colour after UV exposure		Colour change			
1 PMMA	L	83.3	L	84.208	Δ L	0.908	Δ E	2.96
	a	0.798	a	-0.018	Δ a	-0.816		
	b	-0.054	b	2.64	Δ b	2.694		
2 (control Vertex™)	L	82.382	L	79.942	Δ L	-2.44	Δ E	8.72
	a	0.736	a	0.158	Δ a	-0.578		
	b	1.446	b	9.8	Δ b	8.354		
3 PEGMEA	L	84.982	L	82.97	Δ L	-2.012	Δ E	9.28
	a	0.508	a	-0.27	Δ a	-0.778		
	b	1.8	b	10.828	Δ b	9.028		
4 PEGMEMA	L	85.988	L	82.634	Δ L	-3.354	Δ E	11.36
	a	0.764	a	-0.442	Δ a	-1.206		
	b	1.44	b	12.512	Δ b	11.072		
5 EGDMA	L	83.712	L	82.202	Δ L	-1.51	Δ E	8.17
	a	0.482	a	-0.16	Δ a	-0.642		
	b	1.388	b	9.396	Δ b	8.008	Δ E	7.48
6 EGDMA	L	85.516	L	89.104	Δ L	3.588		
	a	0.572	a	-0.434	Δ a	-1.006		
	b	4.24	b	10.726	Δ b	6.486		

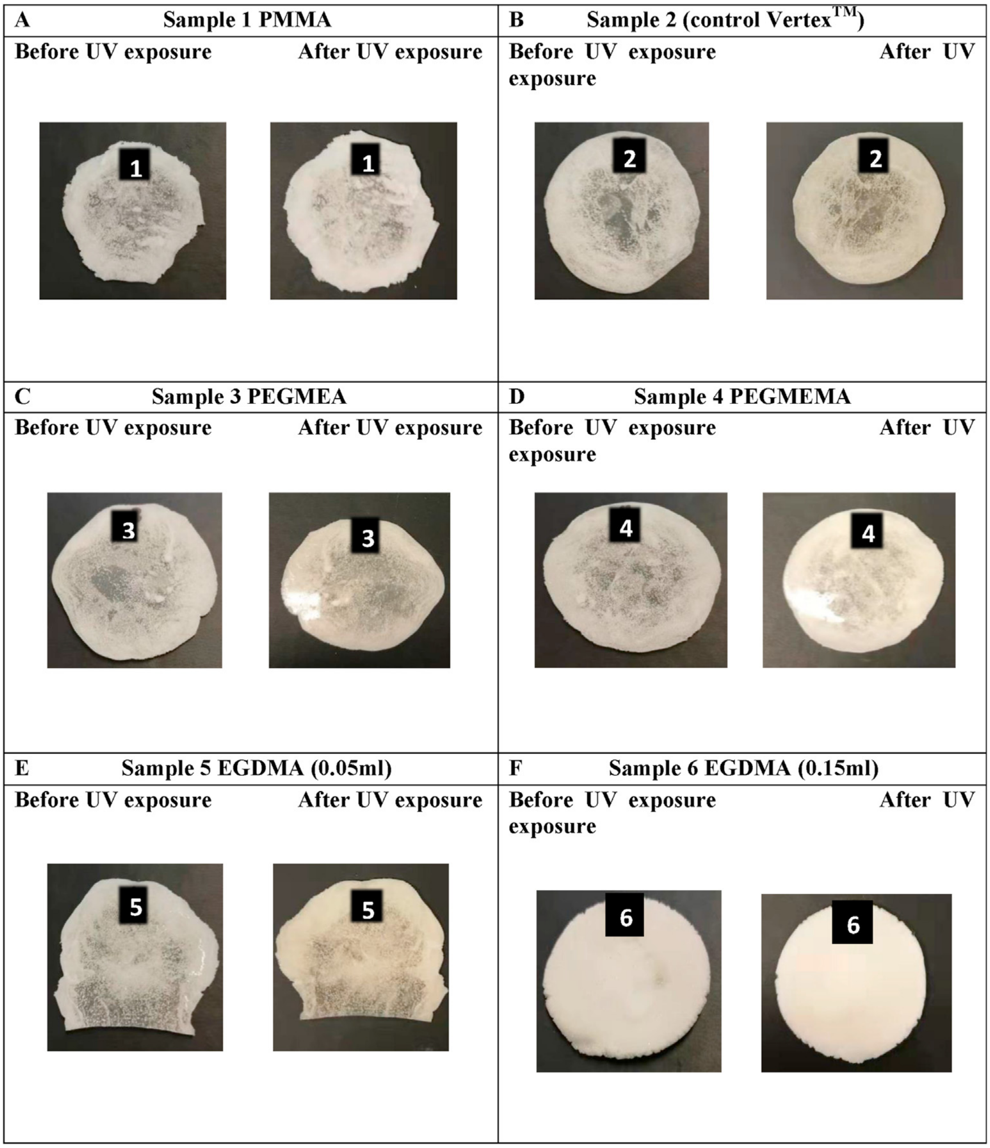

Figure 5. Colour change after 100 h QUV testing: Panel A. pure PMMA sheet, Panel B. PMMA sheet provided by Vertex Dental, Panel C. PMMA grafted with 3.35 wt.% of PEGMEA, Panel D. PMMA grafted with 3.35 wt.% of PEGMEMA, Panel E. PMMA grafted with 1.62 wt.% of EGDMA. Panel F. PMMA grafted with 4.89 wt.% of EGDMA.

increasing EGDMA content. Furthermore, the EGDMA-grafted PMMA matrix altered in colour less than the other PEG derivatives when exposed to intense UV light over 100 h, and the colour-difference was no worse than the Vertex™ control which is currently used for manufacturing PMMA prosthetic eyes. Another advantage of EGDMA for prosthetic eye use over the other derivatives was that Vertex™ monomer already contains EGDMA and the biocompatibility, cost and the toxicity have been already assessed [15, 16]. Thus, further detailed grafting attempts were conducted using polymerized Vertex™ acrylic samples containing different ratios of EGDMA.

The addition of EGDMA up to a proportion of 40% caused a significant decrease in water contact angle but the effect leveled off between 40% and 50% EGDMA. The addition of more EGDMA in the monomer mix produced a less marked difference in contact angle and water absorption measures. A 50/50 mix of EGDMA and Vertex™ monomer (or a 45/55 mix of EGDMA and pure MMA monomer) reduced the initial and static contact angles of clear polymerized PMMA to below 50°. This is a 33% improvement in wettability compared with the Vertex™ mean static angle of 78.8° (SD = 5.02°) and the mean contact angle of 71.9° (SD 9.2°)

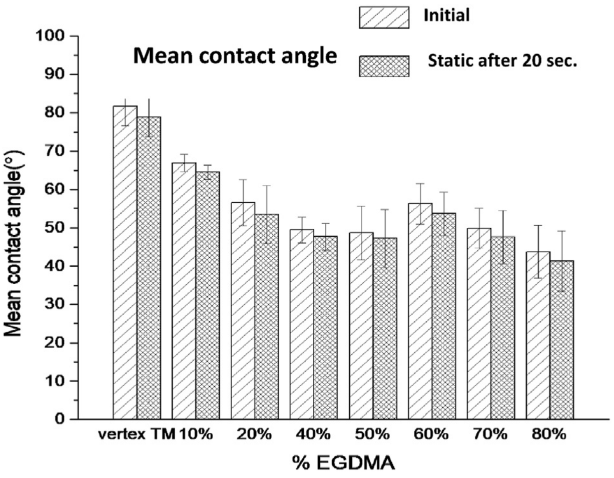

Figure 6. Mean water contact angles as a function of % EGDMA.

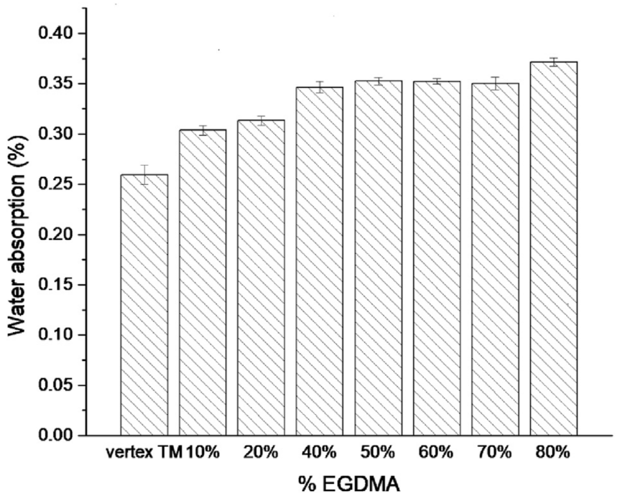

Figure 7. Water absorption as a function of % EGDMA.

achieved by optical grade contact lens polishing on Vertex™ acrylic reported by Pine et al. in 2013 [31].

The EGDMA-grafted PMMA material developed in this research is a practical solution to the problem of PMMA hydrophobicity. Other solutions have been found in the past. For instance, a hydrophilic coating system (BioCoatTM OPT Ocular Prothesis Treatment) was introduced to the market some 30 years ago by BioCoat Incorporated [32] but the time taken to apply the coating was not cost-effective, and the product was subsequently withdrawn. Hydrophilic coatings, developed for contact lenses may also be applied successfully to prosthetic eyes but the application process has strict safety requirements not usually found in the clinics of ocular prosthetists. Glass eye manufacturers have consistently promoted the hydrophilic properties of glass eyes as a point of difference with PMMA prosthetic eyes [33] and while glass eyes appear to be more comfortable to wear they have significant drawbacks in other areas and PMMA is the material of choice for prosthetic eyes globally.

Previous research has shown that surface hydrophilicity of PMMA is influenced by the standard of surface polish and that an optical quality contact lens standard of polish delivers better wettability than other polishes [31] and results in more comfortable prosthetic eyes [34]. However, these prosthetic eyes require regular re-polishing and are significantly more hydrophobic than EGDMA-grafted PMMA prosthetic eyes.

An optical grade contact lens polishing standard improved wettability when applied to Vertex™ PMMA [30] but had no effect when applied to 50% EGDMA grafted to Vertex™ PMMA. Interestingly, the contact angles achieved by the different polishing standards (low, medium & high) negatively corresponded with water absorption measures suggesting that surface texture and water absorption are likely to be related. This would account for the higher water absorption rate of the unpolished samples used to compare PEG derivatives. It is important to note that water absorption was very low in all materials tested and any potential effect that water absorption might have on dimensional stability, plasticity or strength would not affect the application of 50% EGDMA to prosthetic eyes. Further, it is known that crosslinking PMMA, by addition of a compound such as EGDMA yields a more ductile polymer which helps to reduce the brittleness of PMMA polymer [35].

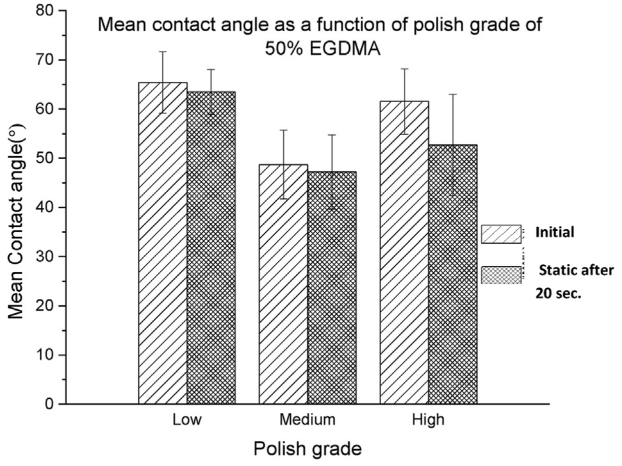

Figure 8. Mean contact angles as a function of polish grade of 50% EGDMA.

In summary, different PEG derivatives were grafted to PMMA matrix using copolymerisation. The resulting matrixes were investigated by water contact angle measurement, 24 h water absorption testing and colour-difference measurement when exposed to intense UV light. The contact angle and water absorption results indicated that EGDMA-grafted PMMA matrix had a better hydrophilic performance than other matrixes tested and when the proportion of EGDMA as a function of liquid PMMA monomer was increased to 50/50 in the manufacture of solid PMMA, the hydrophilicity of the matrix was significantly improved.

EGDMA-grafted PMMA is inexpensive and comes as a liquid monomer that is easily mixed with the PMMA monomer that ocular prosthetists are familiar with. It requires no special handling beyond the normal safety precautions that apply when using PMMA monomers and polymers.

PMMA prosthetic eyes polished to optical grade contact lens standard have been shown to improve surface wettabity and wearing comfort. However, the prosthetic eyes polished to this standard require regular re-polishing and are significantly more hydrophobic than the EGDMA-grafted PMMA material developed in this study.

5. Conclusion

EGDMA-grafted PMMA appears to be more bio-compatable than PMMA currently used for the manufacture of prosthetic eyes and has the potential to significantly improve wearing comfort and socket health. Further in-vivo tests are planned.

Declarations

Author contribution statement

Keith R Pine: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Karnika De Silva: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Fengqian Zhang: Performed the experiments; Analyzed and interpreted the data.

Janice Yeoman & Robert Jacobs: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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