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Impact of manufacturing technology and material composition on the surface characteristics of hydrogel contact lenses

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Background: Our aim was to investigate the impact of manufacturing method and material composition on the surface characteristics of hydrogel contact lenses.
Methods: Five lens types were examined; three polyhydroxyethyl methacrylate (pHEMA) lenses, each manufactured by a different technique, namely, lathing, spin-casting and cast-moulding, a HEMA/methacrylic acid cast-moulded lens and a HEMA/glycerol methacrylate cast-moulded lens. Six lenses of each type were examined (front and back) using scanning electron microscopy (SEM). Additionally, both surfaces of three lenses from each of the pHEMA lens groups were examined, partially hydrated, using an atomic force microscope (AFM). Qualitative data were gathered for both SEM and AFM studies in addition to root-mean-square (RMS) roughness values for the lenses investigated with AFM.
Results: The surfaces of the lathed lenses were covered in lathing/polishing marks. RMS roughness values for the anterior surface (10.9 ± 4.3 nm) were significantly greater ($p = 0.02$) than those of the posterior surface (9.3 ± 0.8 nm). The two surfaces of the spun-cast lens appeared similar by SEM but AFM RMS roughness values were greater ($p = 0.02$) for the anterior (12.3 ± 1.8 nm) than the posterior (5.8 ± 1.9 nm) surface. Both SEM and AFM showed similar topographic appearances for the surfaces of the cast-moulded pHEMA lens, although RMS roughness values were greater ($p = 0.02$) for the anterior (5.8 ± 0.9 nm) than the posterior (3.9 ± 0.3 nm) surface. All three cast-moulded lenses had more processing debris than the lathed and spun-cast pHEMA lenses. Overall, the surfaces of the lathed lens were 'rougher' than those of the cast-moulded lens ($p = 0.01$).
Conclusion: The surface topographies of the hydrogel contact lenses are dependent on the method of manufacture. Cast-moulded lenses are associated with apparently 'stickier' surfaces, which may be indicative of surface degradation during the manufacturing process.

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Key words: atomic force microscopy, contact lens, hydrogel, manufacture, scanning electron microscopy, surface topography

Polymer surfaces and, in particular, hydrogel surfaces are highly sensitive to the processing and fabrication conditions to which they are subjected.[1,2] The surface characteristics of a hydrogel lens will directly affect its interaction with the tear film and consequently its biocompatibility in the ocular environment.[3]

It is possible to study various aspects of contact lens surfaces when addressing questions of ocular biocompatibility; these include the physico-chemical properties[1,2,4,5] of lens surfaces, lens wettability,[6,7] spoilation,[8-10] surface mechanical properties[11,12] and the quality of the surface. The last property can be assessed by viewing the surface at high magnification. Such surface imaging has been achieved by

Material	HEMA	HEMA	HEMA	HEMA/MAA	HEMA/GMA
FDA group	I	I	I	IV	II
Water content (%)	38	39	38	53	60
Manufacturing method	Lathed	Spun-cast	Cast-moulded	Cast-moulded	Cast-moulded
Back surface design	Spherical bicurve	Aspheric monocurve	Spherical monocurve	Spherical monocurve	Spherical monocurve
Dk (cm^2 x mlO_2) / (sec x ml x mmHg)	10	10	10	17	21
Harmonic average thickness (6 mm zone) (mm)	0.08	0.11	0.06	0.10	0.10
BVP (D)	-3.00	-3.00	-3.00	-3.00	-3.00
Base curve (mm)	8.70	Aspheric (8.70 equivalent)	8.70	8.70	8.70
Diameter (mm)	14.00	14.00	14.00	14.00	14.00

HEMA: hydoxyethyl methacrylate; MAA: methacrylic acid; GMA: glycerol methacrylate; FDA: US Food and Drug Administration; BVP: back vertex power

Table 1. Lens specifications

Material	HEMA	HEMA	HEMA	HEMA/MAA	HEMA/GMA
Manufacturing method	Lathed	Spun-cast	Cast-moulded	Cast-moulded	Cast-moulded
Chemical composition	HEMA Low cross-linker Thermal initiator	HEMA Low cross-linker UV initiator	HEMA High cross-linker Thermal initiator	HEMA/MMA High cross-linker Thermal initiator	HEMA/GMA High cross-linker Thermal initiator

HEMA: hydoxyethyl methacrylate; MAA: methacrylic acid; GMA: glycerol methacrylate; FDA: US Food and Drug Administration; BVP: back vertex power

Table 2. Chemical compositions

light, electron[13,14] and atomic force microscopy.[12,15,16]

Factors that are likely to influence surface morphology include the chemical composition of the material from which the lens is fabricated and the method used to manufacture the lenses. Clearly, the way in which the lenses are used, in terms of lens handling and the care regimens adopted, will also have an impact on the surface characteristics of contact lenses.

Currently, the three methods available for soft contact lens manufacture are lathe-cutting, spin-casting and cast-moulding. The method chosen for the manufacture of a particular lens type is usually based on commercial considerations and the wear modality of the lens being made. Lenses fabricated by these different methods of manufacture will undergo very different material processing, particularly polymerisation.[17] These different material processing steps can impact clinical performance (for example, lens fitting and deposition)[18] as well as physico-chemical characteristics (for example, lens surface form and mechanical properties).[19]

Usually, lathed lenses are formed from solid buttons of dehydrated material. In general, buttons are bulk polymerised over relatively long periods in heated water baths or ovens (for 24 to 48 hours). Thermal initiators that have low activation energies are often used; therefore, water baths or ovens can be set to relatively low temperatures. This is likely to result in a polymer structure consisting of longer chains (higher molecular weights) and, therefore, more chain entanglements.

During polymerisation, the walls of the button mould may hinder the supply of fresh monomer to the growing polymer chains. This may decrease the molecular weight at the surfaces of the button relative to the bulk. In addition, oxygen acts

Manufacturing method	Polymerisation conditions
Lathing	Dehydrated solid buttons formed. Thermal initiators with low activation energies. Oxygen scavengers used in a water bath. Twenty-four hour polymerisation time. Diamond tools. Surfaces discarded during lathing. Post-annealed.
Spin-casting	Diluent used. Anaerobic conditions. Fast polymerisation (approximately one hour) using photo-initiators. PVC* casts.
Cast-moulding	Aerobic conditions using thermal initiators. Fast polymerisation (approximately one hour), polypropylene casts.

* PVC: poly vinylchloride

Table 3. Polymerisation conditions

as an inhibitor of polymerisation as the oxygen molecule is a di-radical, which readily combines with initiator radicals during the polymerisation process to form unreactive species. Any oxygen present in the water bath or oven may interact at the surface, which can lead to further degradation. However, the surface of the button is lathed away during lens fabrication, thus reducing the effects of such surface degradation.

During the spin-casting process a mixture of monomers is injected into a spinning mould, which is rotated at a computer-controlled speed. The centrifugal force causes the monomer to rise up the walls of the mould to form the required shape while the lens is polymerised. Additionally, a diluent may be incorporated into the monomer mixture; this promotes more complete polymerisation as the monomers have better access to the growing polymer chains. The diluent also assists in demoulding and can be used to change the swell factor of the material.

Spin-casting is often conducted under anaerobic conditions (that is, the spinning machinery is nitrogen purged) to reduce the surface degradation effects that would take place in the presence of oxygen. This is an important consideration as these surface degradation effects cannot be removed as occurs in the lathing process. Compared to button manufacture in the lathing process, spin-casting is very fast, usually taking less than one hour to polymerise the final lens. The polymerisation is initiated by ultra violet (UV) radiation.

Cast-moulding involves the introduction of a small amount of monomer between two casts to directly form the lens. The polymerisation process is very fast, which is one of the reasons why this is the main method of choice for bulk (disposable) lens manufacture. Rapid polymerisation times are likely to produce shorter chains, more chain ends and less efficient or incomplete cross-links. If the procedure is carried out in the presence of oxygen, then some oxygen may diffuse through the casts and further degrade the surface of the lenses. As is the case with spun-cast lenses, this degradation cannot be removed. Polymerisation of the lenses in anaerobic conditions is likely to reduce these surface effects.

The aim of this work was to investigate the differences in surface topography of:

1. hydrogel lenses manufactured by the three manufacturing techniques described above
2. hydrogel lenses manufactured by cast-moulding using three different materials.

METHODS

Lenses

The experimental lenses used in this work were made using three different manufacturing techniques (lathing, spin-casting and cast-moulding) and were fabricated from three different materials (Tables 1, 2 and 3) at a single contact lens manufacturing facility. Five lens types were used in this investigation. The lenses represented materials from FDA groups I, II and IV. Group III lenses were not investigated, as these are rarely used in contact lens manufacture. The lens types chosen allowed manufacturing method and material type to be investigated as independent variables.

All lenses were supplied in identical glass vials, which contained 0.9% physiologic saline (no surfactant) and arrived randomised-coded from the manufacturing facility. None of the lenses was tinted. All of these features helped to maintain masking during the investigation.

Lens surface imaging

The techniques of scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to image the surfaces of the lenses described above.

SCANNING ELECTRON MICROSCOPY

Six lenses of each of the five lens types were examined using SEM. As this is a destructive technique, three back surfaces and three front surfaces of each lens type could be examined. Sample preparation was carried out using a formaldehyde-free method.[20] The lenses were prepared in accordance with the procedure described by Koizumi and colleagues,[21] in which the lenses were dried by evaporation of hexamethyldisilazane (HMDS). This method produces less sample distortion than other techniques and results similar to critical point drying.[22]

The lenses were removed from their sealed vials and washed in phosphate buffered saline (PBS), under gentle agitation for 15 minutes. They were fixed in 3% aqueous EM grade glutaraldehyde for one hour. Following rinsing with PBS, the lenses were post-fixed in two per cent osmium tetroxide, rewashed in PBS and dehydrated using a series of graded alcohols. The lenses were transferred to HMDS and allowed to air dry. When dry, they were mounted on aluminium stubs, exposing either the front or back surface. Compressed gas was used to remove surface dust from the lenses and they were then gold-coated by vacuum sputtering.

The lenses were observed using a Hitachi S520 SEM (Hitachi Instruments Inc, CA, USA). An acceleration voltage of 10 to 20kV was used,[23] taking care to avoid specimen damage caused by a prolonged stationary electron beam at high magnifications. Images of the centre and periphery (at approximately four locations around the lens circumference and approximately three millimetres in from the lens edge) of both surfaces of each of the five lens types were captured with a digital image capture system.

ATOMIC FORCE MICROSCOPY

The AFM used in this work was a Nanoscope III (Digital Instruments, Santa Barbara, USA), operated in tapping mode[24] with a silicone nitride cantilever. A detailed account of the instrument and its operation has been presented elsewhere.[16,25] Briefly, tapping mode is a variation of the contact mode, where a stiff cantilever is oscillated at its resonant frequency with high amplitudes allowing it to touch the sample during oscillations. Highly sensitive photodiodes allow the detection of amplitude variations by the corresponding deflections of a laser beam.

Three lenses from each of the three pHEMA materials (lathed, spun-cast and cast-moulded) were investigated. The front and back surfaces of each lens type were examined in a semi-hydrated state, that is, the lenses were removed from their vials, desalinated in de-ionised water and mounted onto an electrically grounded magnetic disc. The lens and disc were placed on top of the piezoelectric transducer and the probe tip was run into contact with the lens surface. Previous work has shown that there is a marked difference in the topography of hydrogels in the hydrated and dehydrated states.[1] The difference in z-height (vertical distance between peaks and troughs) has been shown to be greater in the former state.

The Digital Instruments' software was used to produce root-mean-square (RMS) roughness measurements for each lens surface. This is the standard deviation of the z values within a given area (in this case, 50 µm x 50 µm).

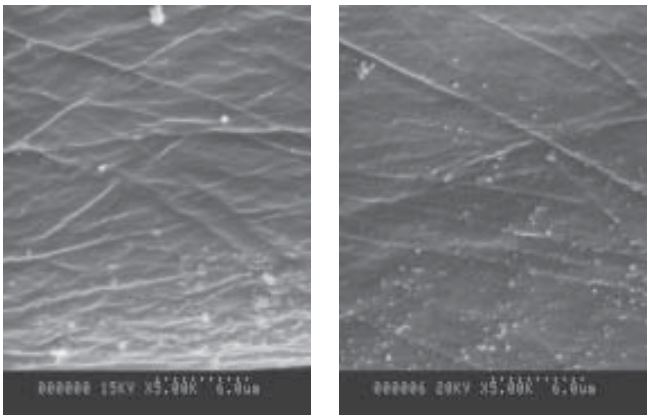

Figure 1. Scanning electron micrograph of the front surface (left) and back surface (right) of the lathed pHEMA lens. Original magnification x5000.

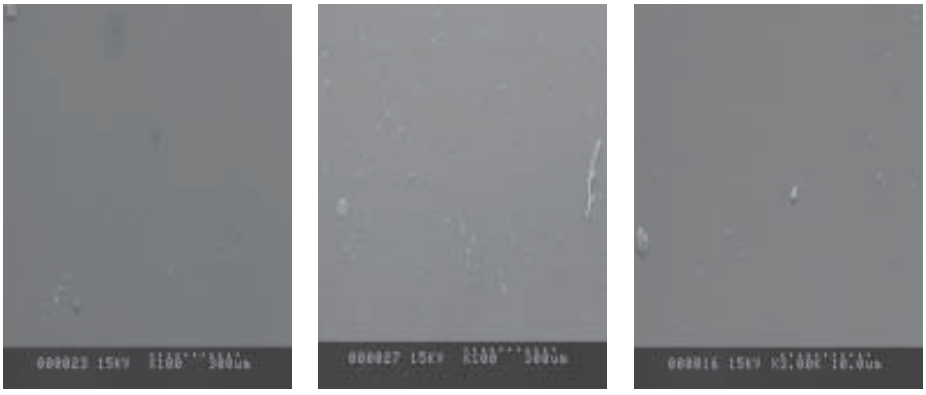

Figure 2. Scanning electron micrograph of a spun-cast pHEMA lens. Front surface (left) (original magnification x100), back surface (centre) (original magnification x100) and high magnification front surface (right) (original magnification x3000).

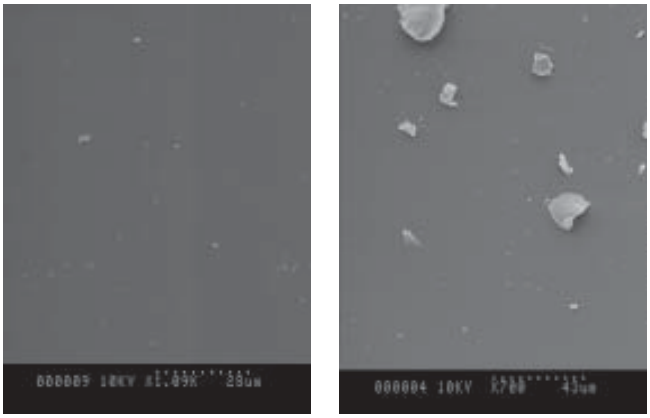

Figure 3. Scanning electron micrograph of the front surface (left) (original magnification x1090) and back surface (right) (original magnification x700) of a cast-moulded pHEMA lens

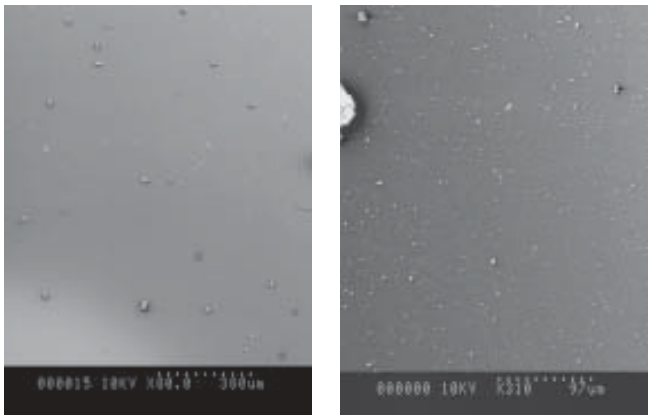

Figure 4. Scanning electron micrograph of the front surface (left) (original magnification x80) and back surface (right) (original magnification x310) of a cast-moulded HEMA/MAA lens

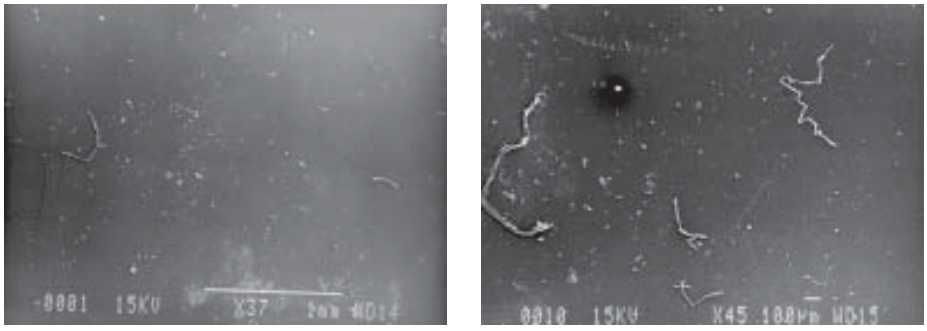

Figure 5. Scanning electron micrograph of the front surface (left) (original magnification x37) and back surface (right) (original magnification x45) of a cast-moulded HEMA/GMA lens

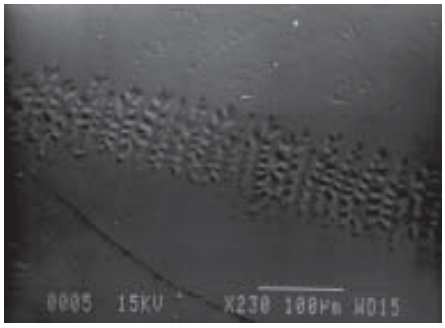

Figure 6. Scanning electron micrograph of lens shrinkage marks on the front surface of a HEMA/GMA lens. Original magnification x230.

Data analysis

Results for the SEM work were qualitative and therefore no statistical analysis was carried out.

The AFM RMS roughness data set was checked for normality using the Kolmogorov-Smirnov test.[26] A p value of greater than 0.99 was obtained, indicating that it was appropriate to use parametric statistical analysis to investigate the lens surface roughness. A factorial analysis of variance (ANOVA) was employed with lens type and surface (anterior or posterior) used as factors. A p value of 0.05 was taken to be the threshold for statistical significance. Any statistically significant differences were further investigated using Tukey-Kramer *post hoc* analysis.

RESULTS

Scanning electron microscopy

The typical appearance of the surfaces of a lathed pHEMA lens is shown in Figure 1. Both front and back central lens surfaces appeared similar, showing criss-cross lathing/polishing marks. The only difference noted between the front and back surfaces was that the front surface had a higher concentration of polishing marks near the periphery. This was probably due to the increased polishing the lens was known to have received at the edges.

Figure 2 shows the surfaces of a typical spun-cast pHEMA lens. Both surfaces appeared smooth. The front surface appeared very clean and free from dust and processing debris when compared to the back surface. No differences were apparent between the two surfaces at the lens periphery.

Representative surfaces of a cast-moulded pHEMA lens are presented in Figure 3. These appeared smooth but both surfaces were coated with more dust and processing debris than either the lathed or spun-cast pHEMA lenses. Both surfaces were coated to a similar degree. The surfaces of the cast-moulded HEMA/MAA lens (Figure 4) appeared similar to each other in morphology. Dust and processing debris were observed on both lens surfaces to a similar extent as that seen on

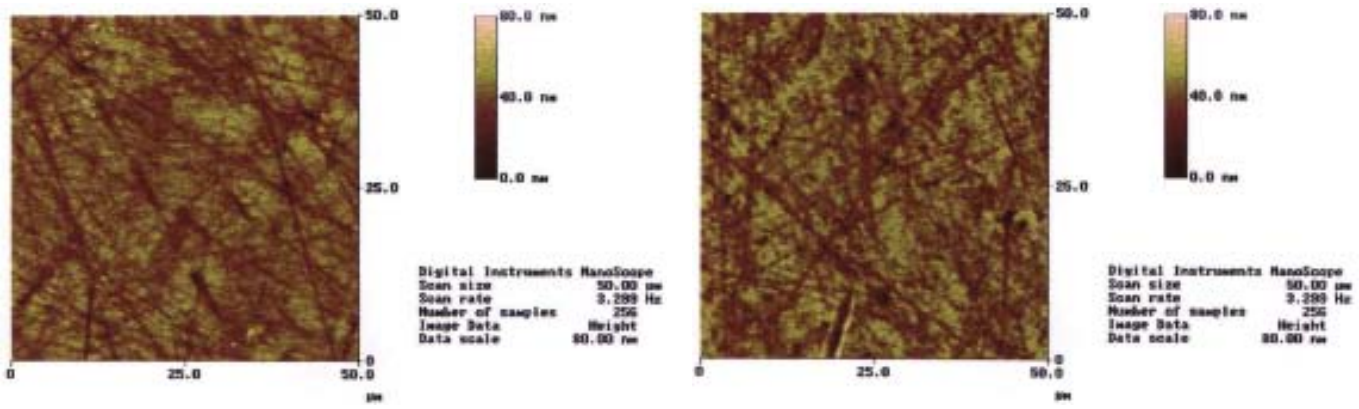

Figure 7. AFM of anterior (left) and posterior (right) lens surfaces of a lathed pHEMA lens. 50 μm scan.

Lens type	Posterior surface (nm)	Anterior surface (nm)
pHEMA lathed	9.27 ± 0.80	10.89 ± 4.33
pHEMA spun-cast	5.77 ± 1.89	12.27 ± 1.75
pHEMA cast-moulded	3.94 ± 0.28	5.79 ± 0.93

Table 4. RMS roughness values (mean ± SD) for the anterior and posterior surfaces of the pHEMA lenses (50 μm x 50 μm).

the cast-moulded pHEMA lenses. The surfaces of the cast-moulded HEMA/GMA lenses displayed the greatest amount of dust and processing debris (Figure 5).

Methodological problems were encountered during this work when examining the HEMA/GMA lenses. Specifically, these lenses were observed in real time to crack and degrade when imaged at high magnification, even for very short periods of time, presumably as a result of the necessity to impart a higher energy electron beam under such conditions. This degradation took the form of dimple or bubble-like inclusions (approximately 5 mm in diameter) within the material; this type of technique-induced degradation did not occur with the other lens types.

A form of stippling was observed on the front surface of the cast-moulded HEMA/GMA lens near the lens periphery (Figure 6). This appearance was noted on two of the three lenses and is thought to represent shrinkage marks occurring during the cast polymerisation process. These markings were not seen with any of the other cast-moulded materials and therefore, are unlikely to have resulted from the SEM sample preparation process.

Atomic force microscopy

The quantitative data from the RMS roughness evaluation are summarised in Table 4. Statistical analysis showed that surface was a significant factor in the analysis ($F = 8.4$, $p = 0.02$); the anterior surfaces being rougher than the posterior surfaces for all of the three pHEMA lenses (the lens type x surface interaction was not statistically significant). The surfaces of the lathed lens were rougher than the surfaces of the cast-moulded lens ($F = 7.7$, $p = 0.01$). There were no other significant differences in roughness between lens types.

Once again, the lathed surfaces appeared to be covered with lathing and polishing marks (Figure 7). The depth of the scratches was in the region of 50 nm. The topographies of the two surfaces appeared similar despite the differences in the roughness observed.

The roughness results for the anterior spun-cast pHEMA lens surface were unexpected, as the anterior surface had a roughness similar to that of the lathed surfaces. The AFM images (Figure 8) show a clear difference between the topography of the two surfaces.

AFM images of the surfaces of the cast-moulded pHEMA lens are shown in Figure 9. The topographies of the two surfaces appeared similar despite the differences in the roughness observed.

DISCUSSION

Scanning electron microscopy

The results of this work demonstrate that lens surfaces produced by lathing are markedly different from those produced by cast-moulding and spin-casting. The lathing/polishing marks observed on the lathed lenses in this study are similar to those previously reported.[13,14,27,28] SEM did not show any marked difference between the surface morphology of the spun-cast and cast-moulded lenses—both appeared smooth. Using SEM, earlier studies[28] on new, unworn lathed lenses have noted granular deposits that have been attributed to polishing debris. It is not possible to deduce the origin of a particular type of debris observed using SEM. During this

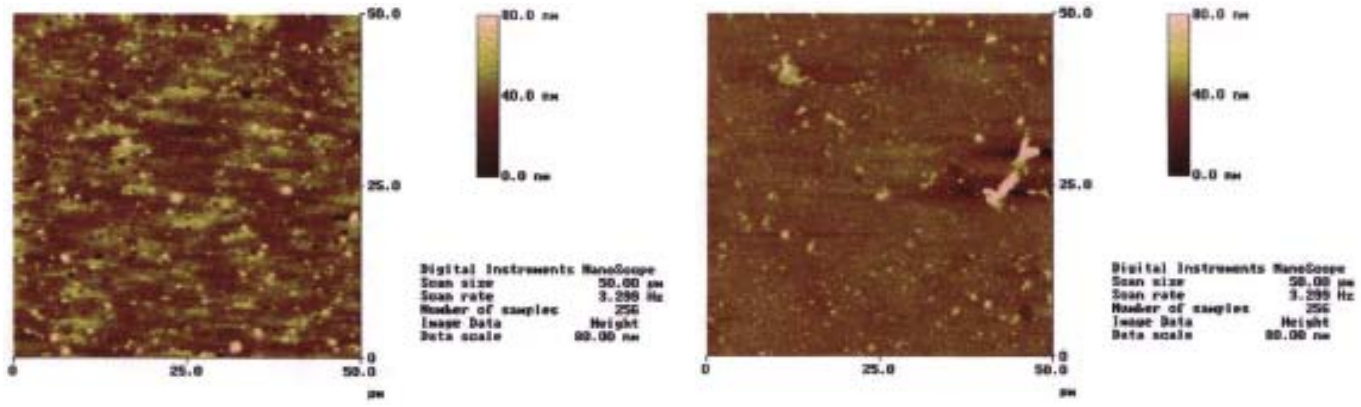

Figure 8. AFM of anterior (left) and posterior (right) lens surfaces of a spun-cast pHEMA lens. 50 µm scan.

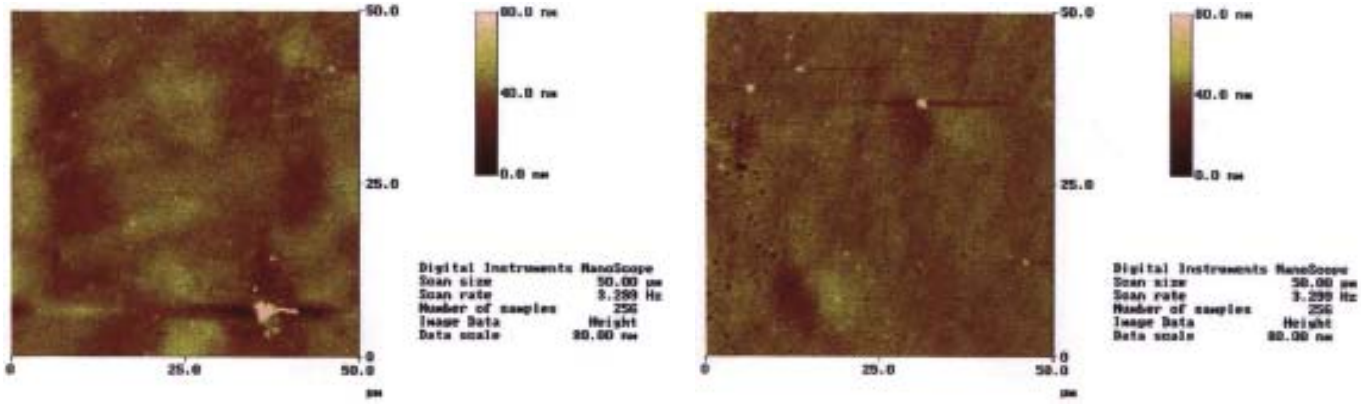

Figure 9. AFM of anterior (left) and posterior (right) lens surfaces of a cast-moulded pHEMA lens. 50 µm scan.

work, debris of unknown origin was seen in varying degrees on all of the lenses investigated.

Surfaces produced by the same method (for example, the front and back surfaces of the lathed lens and the front and back surfaces of the cast-moulded lenses) appeared essentially the same when imaged with the SEM. It is interesting to note that the surfaces of the lens that had its two surfaces formed in different ways, that is, the spun-cast lens, appeared similar except for the fact that more debris was attached to the back surface than the front. The front surface was polymerised against a polyvinyl chloride (PVC) cast and the back surface was polymerised in an environment that was open to nitrogen gas. Although it would follow that being exposed to an open environment, this back surface would have more processing debris attached to it, the possibility that this debris became attached to the lenses after removal from the vial and during the SEM sample preparation process cannot be discounted. The fact that all three lenses examined showed this trend supports the theory that the front surface is likely to be a cleaner surface.

The HEMA/GMA lens surfaces showed higher levels of this attached processing debris than any of the other lens types. In our concurrent clinical investigation[18] using the five lens types examined in the present work, it was observed that when the HEMA/GMA lenses began to dehydrate, they stuck together readily and were very difficult to pull apart without tearing. These lenses attracted the lowest scores for ease of handling and were recorded as the most frequently torn lenses. The cause of these sticky surfaces is thought to lie in the way that the lenses were polymerised (Table 3). Essentially, the deliberate, non-optimal way that these lenses were manufactured was likely to have promoted non-crosslinked (shorter) chains at the polymer surface. This hypothesis is supported by work carried out using time-of-flight secondary ion mass spectrometry,[2] which investigated the surface molecular

polymer arrangement of the three pHEMA lenses used in the present work. Unsaturated and/or aromatic hydrocarbon species, indicative of surface degradation, were observed only at the surfaces of the cast-moulded lenses. Additionally, Kim and co-workers[12] have reported the presence of non-crosslinked polymer chains at cast-moulded contact lens surfaces, which extend up to 10 nm when immersed in saline solution. These polymer fronds may engulf particles in the tear film, which would have an impact on spoilation and bacterial adhesion. This sort of phenomenon may have been responsible for attracting and attaching the processing debris observed in this study. Further support for this oxygen degradation theory was seen when the same HEMA/GMA monomer mix was cured in exactly the same polypropylene moulds, anaerobically. No sticky surfaces were obtained in the final lenses.[29] This simple example serves to illustrate how the different facets of the polymerisation process may dramatically alter the surface characteristics of a material and shows how these factors are likely to explain some of the differences observed between lenses made by the different manufacturing processes.

SEM is also useful for observing lathe or polishing marks on cast-moulded and spun-cast lenses that have been mirrored in the final lenses from the original metal tool insert. No such surfaces were observed in this study. The only unusual finding was that of the apparent shrinkage marks on the HEMA/GMA lenses. These are likely to have been caused during polymerisation, as the polymer shrank away from the mould or during the demoulding process. Factors such as the rate of heating, cure kinetics, wetting of the mould, the surface degradation occurring and the material used for the cast are all likely to affect the level of shrinkage seen. The HEMA/GMA lens is likely to have been more prone to this shrinkage problem as the material was more hydrophilic than the other materials.

Atomic force microscopy

The RMS roughness values found in the present study are slightly smaller than those published in previous studies,[1,12,25] which may be accounted for by the fact that the lenses in the present study were examined in the partially hydrated state.

The AFM findings highlight the differences between the four types of lens surface and confirms that the topography of surfaces produced by the same method of manufacture are essentially the same. The four surfaces investigated were:

1. lathed (that is, the two surfaces of the lathed lenses)
2. cast-moulded against polypropylene (that is, the two surfaces of the cast-moulded lenses)
3. spun-cast against PVC (that is, the anterior surface of the spun-cast lenses)
4. spun-cast open to nitrogen (that is, the posterior surface of the spun-cast lenses).

SEM showed that the front and back surfaces of the lathed lenses appear similar. The images produced by the AFM also appear similar together with the figures for the RMS roughness (Table 4). Statistically, there was a significant difference between the two surfaces. This difference could have arisen due to small differences in the manufacturing steps taken during lens production. First, the back surface was cut using three different diamond cutting tools, whereas the front surface was formed using only two diamond tools. Different diamond tools at different stages in their life span may produce lenses with differing surface topographies. A diamond cutting tool will generally cut about 7,000 lenses before it needs to be replaced. Second, the back surface was polished for slightly longer than the front surface using a slightly different type of polishing machine. The same polishing mixture was used for both surfaces. These differences could account for the statistically significant difference between the RMS roughness values for the two surfaces of the lathed lenses.

Whereas SEM showed no differences between the cast-moulded lens surfaces and the PVC spun-cast front lens surface, AFM did show differences in topography between these surfaces. Although statistically there was no significant difference in roughness between the anterior surfaces of the spun-cast and cast-moulded lenses, the AFM topographic images and the figures in Table 4 suggest that there may be a trend for the anterior surface of the spun-cast lens to be rougher. The reason for this is unclear. One possible explanation is that surface grafting of the PVC mould to the hydrogel surface occurs during the manufacturing process. As PVC is a partially crystalline polymer, its surface will comprise some crystalline regions separated by amorphous regions. These amorphous regions may become attached to the hydrogel surface and in effect, an imprint of the surface PVC pattern may be formed on the lens surface. As polypropylene was the material for the moulds in the cast-moulded lenses, there may have been different degrees of crystallinity at the mould surfaces, perhaps explaining why this effect was not seen with the cast-moulded lenses. The spinning process itself may also promote surface grafting.

Another explanation for the anterior surface roughness of the spun-cast lens may be that under UV radiation, the PVC produces free radicals. These radicals may bond/graft the monomer to the surface and there may be a tendency to tear the surface when the lenses are demoulded. When PVC is injection-moulded, it can produce hydrochloric acid, which can erode the stainless steel metal insertion (if it is old) used to make the moulds. This may impart a granular character to the insertion surface and ultimately to the lens surface. The results of a previous study have shown that the roughness of the anterior surface of a spun-cast lens is significantly greater than that of lathed lens surfaces and cast-moulded lens surfaces.[25] No explanation of why this occurred was given. As far as we are aware, no other AFM study has investigated the differences in surface topography among the three manufacturing methods.

The SEM and AFM imaging studies presented here have confirmed that lenses made by different manufacturing technologies have different surface topographies. It is important to emphasise that differences observed among different methods of manufacture may be different

under different conditions and in the hands of different laboratories. The results of our clinical work[18] provide some evidence to support the theory that surface topography is related to clinical performance.

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