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Development of novel elastomer/methacrylate monomer soft lining materials

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An earlier study identified a formulation comprising a butadiene/styrene copolymer (PBS) gelled with ethyl hexyl methacrylate (5 + formulation) as a potential denture soft lining material. It had good mechanical properties but water uptake was high as a result of the presence of a separating agent. This study has compared the tensile and water absorption properties of four elastomers free from separating agent (three butadiene/styrene, HBS, EBS, SBS, and one isoprene/styrene, SIS) with those of PBS all using the 5 + formulation. HBS is emulsion polymerized; the others are solution polymerized. SIS5 + had the better tensile properties whereas HBS5 + had the lowest water uptake. All the other 5 + formulations had higher uptakes than PBS5 +, which is thought to be due to the presence of hydrophilic groups from the solution polymerization process. All materials showed some sign of oxidation. Emulsion polymerized elastomers are regarded as less suitable for medical uses than the solution polymerized alternatives. Of these, SIS5 + seems to be less prone to oxidation and has the better mechanical properties so was considered to be the most suitable material for further development.

1. Introduction

Soft lining materials are commonly applied to the fit surface of the mandibular (lower) denture to improve comfort and retention. They also find use as other maxillo-facial prostheses, e.g. cleft palate devices and obdurators [1–3]. Generally, the materials currently available are silicone- or methacrylate-based. The main problem with the conventional methacrylate-based materials is loss of plasticizer leading to gradual hardening in the mouth [4].

One approach to solving this problem is to use an elastomer (usually in powder form) gelled with a methacrylate monomer to produce a soft material without the use of a plasticizer [5]. This method has produced materials which show potential as soft lining materials [6]. A recent study described in detail the water absorption characteristics of a series of elastomer/methacrylate materials using a powdered butadiene/styrene elastomer (PBS). Although these materials had good strength they had high water uptake which was attributed to the presence of a separating agent added in manufacture to stop agglomeration of the PBS particles [7]. Water uptake of elastomers is governed by the presence of water soluble or hydrophilic components, these act as sites for the formation of droplets which grow until restrained by the elastic force of the material. The driving force is the chemical potential gradient between the droplet and the external solution, and the theoretical aspects are well documented [8–11].

PBS is an emulsion polymerized material which is then ground and separating agent added to prevent agglomeration of the particles. Two groups of elastomers are available without separating agent; these are either bulk (or bale) elastomers which, rather than being a powder, are solid uncrosslinked rubbers, or solution (rather than emulsion) polymerized elastomers. These solution elastomers are available as either bales or pellets which do not cluster together as they are block copolymers which are, in effect, cross-linked by the hard domains and as such are not ''sticky''.

It is the aim of this study to evaluate alternative elastomers using the monomer formulation that was found to give the best combination of properties with PBS.

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2. Materials

Three different butadiene styrene and one isoprene styrene copolymers were selected (listed in Table I, specifications given in Table II) as alternatives to the PBS previously used [7]. HBS is polymerized using the 'Hot' emulsion process, this involves free radical initiation at ~ 50 °C and tends to produce a random branched butadiene styrene elastomer [12]. Alternatively, when the polymerization is performed at 5 °C (known as the 'Cold' process) a linear material is produced and the degree of conversion is slightly lower at ~ 60% compared to 72% for the Hot process [13]. The Hot elastomer was chosen for this reason. The other materials were all solution polymerized. SBS and SIS are block copolymers, EBS is a partial block copolymer with 17% of the 25% styrene being in block form. The SIS was only available with 0.2 wt % silica as a dusting agent but it was felt that the silica was present at a low level and, as it is insoluble, should have negligible influence on the uptake.

The elastomers were all used at the 50/50 wt/vol level with the monomer formulation that gave the highest strength when used with PBS. This comprised ethyl hexyl methacrylate with 1% ethylene glycol dimethacrylate and 1% lauryl peroxide; this is designated as the 5 + formulation. Suppliers are listed in Table I.

Gels were prepared by mixing the elastomer with the monomer as above and leaving for 24 h to form a gel. HBS and EBS came as bales and had to be cut into small particles (~5 mm) in order to be dissolved in the monomer. The porous pellets (SBS and SIS) were approximately 3–5 mm diameter which was small enough to form a gel quite readily with the monomer.

3. Methods

3.1. Specimen Preparation

The gels were molded into 1 mm thick sheets between stainless steel plates lined with acetate sheets using a hydraulic press. The molds were clamped and placed in cold water which was then heated slowly over 30 min to boiling and maintained at that temperature for a further 30 min to ensure polymerization.

Sheets of pure elastomer were prepared by casting from a solution of the elastomer in chloroform. All specimens were cut from these sheets.

3.2. Tensile Test

Dumb-bell shaped specimens approximately 70 mm in length with a central section 3 mm wide were cut from the sheets of materials as prepared above. At least 6 specimens of each formulation were tested. A 20 mm length of the central section of each specimen was marked with reflective spots. Specimens were tested in a J&J Instruments tensile testing machine at a machine speed of 500 mm/min. Extension was measured using an infra-red extensometer attachment. Maximum load and extension at break were recorded and used to calculate ultimate tensile strength and percentage elongation at break.

3.3. Water Uptake

Water absorption characteristics of all the materials and the pure elastomers were assessed using specimens approximately $20 \times 40 \times 1\,\text{mm}^3$ cut from the sheets as prepared above.

Specimens were first dried to constant weight in an oven and then immersed in distilled water contained in a sealed glass jar maintained at 37 ± 1 °C. The specimens were removed, blotted on filter paper to remove surface water, and weighed at set time intervals. Two specimens of each were used.

After 196 days, one specimen of each was removed and desorbed in an oven at 37 ± 1 °C, weighings being made at regular intervals. When the specimens had reached minimum weight they were again placed in water as before and weight change monitored.

Plots were made of % weight change against square root time in minutes for both absorption and desorption. Solubility was calculated as the difference in between initial dried weight and minimum desorbed weight as a percentage of initial dried weight.

4. Results

Fig. 1 shows the tensile strength and elongation to break for all the materials tested, showing SBS5 + and SIS5 + to have similar tensile strengths to the original PBS5 +, SIS5 + having the highest elongation to break.

Fig. 2 shows the first water uptake cycle of all the 5 + materials. HBS has the lowest uptake, appearing to reach equilibrium at ~3 wt %. EBS5 + has the highest uptake initially but SIS5 + and SBS5 + have the highest in the later stages. Fig. 3 shows the water uptake of the pure elastomers showing that all the elastomers have a lower uptake than PBS with SIS having the lowest. Fig. 4 shows the first and second water uptake cycles for all the 5 + materials. All have a greater uptake in the second cycle than the first, with SBS5 + having the highest

TABLE I Materials

Material	Supplier	Code
STR 7030	Plascoats Systems Ltd	PBS
S–1013	Shell Chemicals Ltd	HBS
Europrene 1205	Enichem Elastomers Ltd	EBS
Kraton D–1101	Shell Chemicals Ltd	SBS
Kraton D–1111C	Shell Chemicals Ltd	SIS
Ethyl hexyl methacrylate	Bonar Polymers Ltd	EHMA
Ethylene glycol dimethacrylate	Bonar Polymers Ltd	EGDMA
Lauryl peroxide	BDH Chemicals Ltd	LP

TABLE II Specification of the elastomers

	PBS	HBS	EBS	SBS	SIS
Volatile matter, max.	—	1.0%	—	0.3	0.3%
Total ash, max.	—	0.8%	—	—	—
Total extractable, max.	—	—	—	1%	1%
Organic acid	—	3.5–5.5%	—	—	—
Soap, max.	—	0.3%	—	—	—
Silica	—	—	—	—	0.2%
Styrene content	30	41.5–44.5%	25 wt %	31 wt %	22 wt %
Solution	—	—	Hexane	—	—
Antioxidant	—	—	0.5% BHT	1.4% min BHT	1.4% min BHT
Initiator	—	—	Butyl lithium	Alkyl lithium	Alkyl lithium
Density	940 kgm^{-3}	960 kgm^{-3}	—	940 kgm^{-3}	930 kgm^{-3}

BHT = Butadiene hydroxyl toluene (Ionel).

increase and EBS5 + the lowest. Table II shows the solubility and total uptake of all the 5 + materials, with HBS having the highest solubility and SBS5 + having the lowest as a negative indicating an increase in dry weight.

5. Discussion

Fig. 1 shows the tensile results for all elastomer 5 + formulations with similar strengths for SBS5 + and SIS5 + to that of PBS5 +, although SIS5 + has the higher elongation to break and as such will have the highest energy to break. EBS5 + and HBS5 + were, however, considerably weaker than PBS5 +. The reason for this is unknown as it may relate to many factors such as additives (inhibitors) added to the elastomer during production or molecular weight of the elastomer, but the susceptibility to grafting of methacrylate [6] to the elastomer or the homogeneity of the material seem most likely as the EBS and HBS have different structures (as the EBS is a partial block and HBS is branched).

Comparing the water uptake of all the formulations (Fig. 2), HBS5 +, as may be expected from the absence of separating agent, shows a lower uptake than PBS5 + and seems to level off indicating the material is reaching equilibrium. The absence of the separating agent gives a lower uptake so the material behaves in a more ideal manner. The level of uptake still seems rather high and this is likely to be due to the production process of the elastomer. From Table II we can see that there is a portion of soap and organic acid (3.5–5.5%) listed and this will undoubtedly increase the water uptake, particularly at 37 °C. Water uptakes of the solution polymerized materials show a higher eventual uptake than the PBS5 +, although SIS5 + is initially lower. The latter stages when there is an upturn in the water uptake of SBS5 + and SIS5 + is due to oxidation of the elastomer, but the initial uptake and that of the EBS5 + must be due to another factor. Solution polymerized materials are generally regarded as cleaner (less impurities) than the emulsion polymerized materials as they don't contain the organic acids and impurities introduced during the initiation process. However, they are anionically polymerized which will leave active radicals at the chain ends after polymerization. These are then available to form hydroxyl groups if exposed to water or, perhaps more likely, carboxylic acid if exposed to carbon dioxide. These carboxylic acid and hydroxyl groups will have an effect on the water uptake. There will be other components within the polymer which may influence the water uptake such as the antioxidant and the initiator (e.g. alkyl lithium compounds such as butyl lithium). It is, however, felt that the action of these elements which will be present at low levels (under 2% for the antioxidant, BHT, and much less for the initiator) will be insufficient to account for the water uptake of over 6% (as they are organic rather than inorganic) observed for these materials (which is higher than the PBS5 + material containing the separating agent). SBS5 + and SIS5 + have a higher proportion of BHT than EBS5 + yet show a lower uptake. This supports the hypothesis that the BHT is not responsible for this

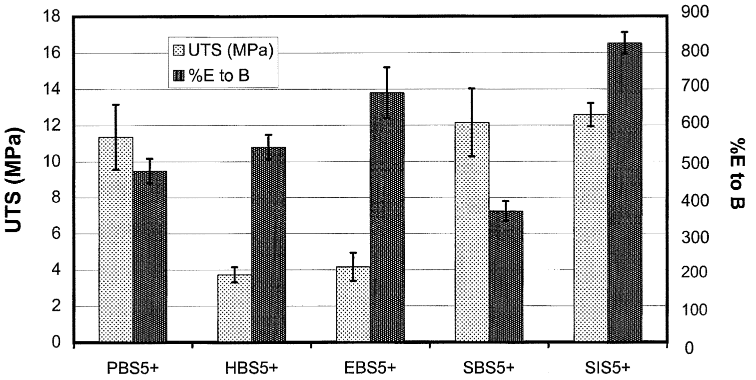

Figure 1. Tensile data for all 5 + formulations.

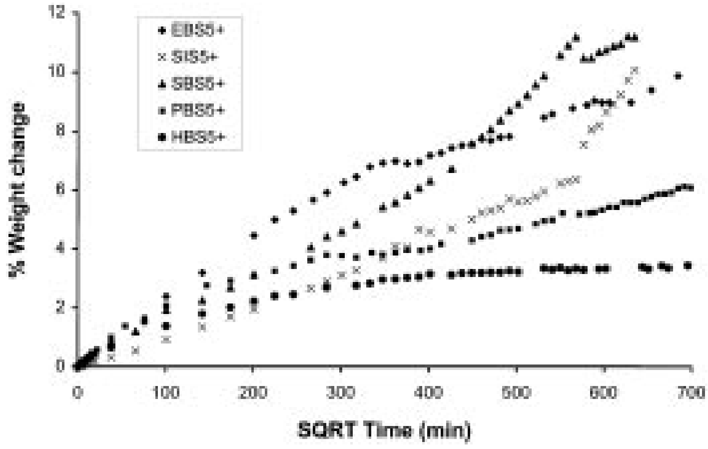

Figure 2. First water uptake cycle of all 5 + formulations.

uptake. It is therefore felt that the water uptake for the solution polymerized materials is due primarily to the carboxylic acid and hydroxyl end groups on the elastomer. The uptake of water into the elastomers was accompanied by opacity, indicating the formation of droplets within the material. This is due in turn to light scattering, which will occur if the size of the droplets is of the order of the wave-length of visible light. In the absence of a satisfactory hydrophilic constituent, a clustering of these hydrophilic groups seems the most probable cause. If the groups were acting independently the uptake would be expected to be uniform and hence the material would remain transparent.

Fig. 3 shows the uptakes of the cast elastomers, where there are striking similarities between all the elastomers (apart from the later stages where oxidation seems to predominate) except the PBS which shows a slightly higher uptake. This is in contrast to the results of the 5 + samples in Fig. 2 where different absorption characteristics are seen for the different materials. This seems to imply that the driving force behind the water uptakes (i.e. water soluble or hydrophilic components) are similar in each elastomer, suggesting the restraining force exerted by HBS5 + is greater than that of EBS5 + (as it shows a lower uptake). The strength results imply this is not the case as EBS5 + exhibits a slightly higher UTS so another factor seems responsible. It is impossible to know what is driving the uptake and why they differ but a few points can be made.

The cast elastomers are uncrosslinked and so will flow and facilitate droplet growth, whereas the 5 + samples will be slightly cross-linked hence should creep less resulting in a better restraint of droplet growth. Stress relaxation will decrease the restraining force and so increase the effective driving force behind the uptake. As the uptake occurs over an extensive period it is likely that the restraining force in the cast elastomers will be insufficient to prevent the continued growth of the droplets. The absorption will then become more dependent on the rate of transfer of water into the material as the driving force is sufficient to ensure that this rate of ingress is determined by the diffusion coefficient. The nature of the impurity will also be less important as it does not have to overcome the restraining force. It is therefore proposed that HBS5 + contains an impurity which generates a less effective driving force, either by being present in smaller concentrations or having a higher molecular weight, than EBS5 + hence is more readily restrained. When the materials are uncrosslinked this difference is less significant as the absence of an effective restraining force makes the nature of the driving force less important.

A summary of the absorption data is shown in Table III, with EBS5 + and SIS5 + having very low

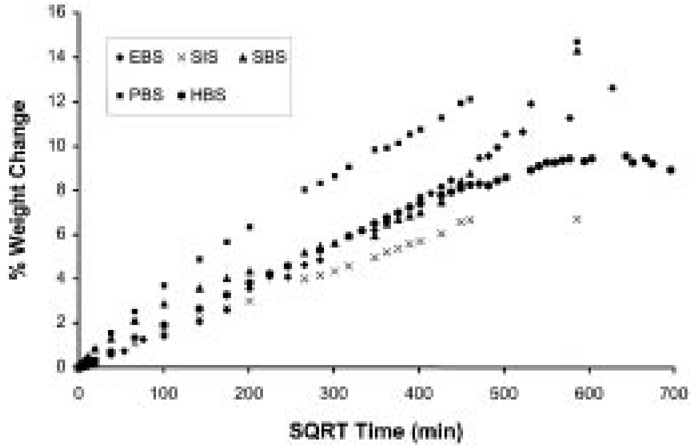

Figure 3. Water uptake of pure elastomers.

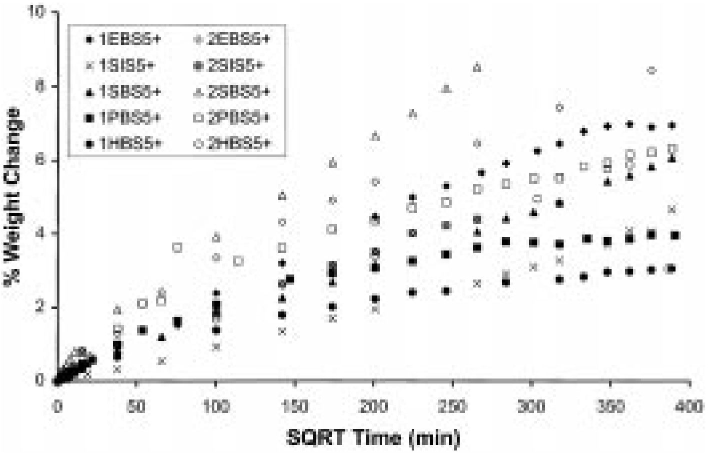

Figure 4. First and second water uptake cycles of all 5 + formulations.

solubilities compared to the HBS5 + and PBS5 +. SBS5 + shows an increase in weight after desorption, indeed the weight increases during the desorption cycle with a minimum solubility of − 0.85 wt % being indicated. This behavior seems to be due to oxidation of the elastomer.

The second absorption cycles for these materials (Fig. 4) show the familiar pattern with the water uptake being higher and more rapid. This is due to the deformation around the droplets which occurred during the first sorption cycle making the growth of these droplets easier. The oxidation of SBS5 + has caused a massive increase in rate and quantity of water absorbed into the polymer due to the hydrophilic nature of the groups produced.

All the materials showed some sign of the oxidation process although some showed a greater resistance than others. In addition to the oxidation process being accompanied by an increased water uptake there was a discoloration (yellow to brown) of the sample, this initially occurred at the edges then slowly moved throughout the sample, a hardening of the material was also observed. The oxidation of elastomers can occur by many different mechanisms depending on the material and the environment. Generally diene (or vinyl) bonds [12] are attacked but other groups (e.g. styrene) are also prone to attack, the basic mechanism being a free radical auto catalytic process forming hyperoxides. A widely used means of preventing oxidiation is to employ an antioxidant. These work in many different ways but in general they accept the radical and trap it to form a stable radical. The major problem with antioxidants is their tendency to leach out of the material; also the antioxidant will eventually get used up and so the oxidation resistance has a limited life. Such must be the case here. Also there is the question of the toxicity of the antioxidant.

HBS5 + had the most promising water uptake and relative resistance to oxidation. However, emulsion polymerized elastomers have attracted a reasonable level of concern over their potential toxicity (due to their high extractable content) and are generally regarded as less suitable for food and medical uses than the solution polymerized alternatives [14]. For this reason, and its relatively low tensile properties, the HBS was thought to be unsuitable as a potential soft lining material. The solution polymerized materials exhibited a surprisingly high water uptake, all showing some sign of oxidation in distilled water. However, they are thought to be better from a biological context and the SIS seems to be less prone to oxidation. Comparison between the SBS and SIS is interesting as both contain the same proportion of antioxidant (Table II) but the SIS shows a much slower rate of oxidation (Fig. 2). This is thought to be the steric hindrance of the extra methyl group on the isoprene compared to the butadiene. For this reason, and the better mechanical properties, SIS was thought to be most suitable for use as a soft lining material although further development to further reduce water uptake and tendency to oxidise is required.

6. Conclusions

Factors other than the presence of a separating agent were found to affect the water uptake of these materials.

SIS proved to be the most suitable elastomer for use as a soft lining material although further development is required.

TABLE III Summary of water uptake data

Material	Absorption, wt %	Solubility, wt %	At, days	Total Uptake, wt %	2nd ab wt %	At, days
HBS5 +	3.22	0.62	210	3.84	6.70	126
EBS5 +	8.71	0.00	203	8.71	20.40	238
SIS5 +	5.96	0.14	217	6.11	4.40	49
SBS5 +	11.08	− 2.95	217	8.13	8.54	49
PBS5 +	4.84	0.38	196	5.22	16.87	399

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