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Effect of composition on the mechanical properties and water sorption of a butadiene/styrene copolymer-methacrylate monomer soft lining material

S. PARKER*, P. RIGGS
Dept. of Biomaterials in Relation to Dentistry, London Hospital Medical College, Turner Street, London E1 2AD, UK

S. KALACHANDRA
Chemistry Dept., Virginia Polytechnic and State University, Blacksburg, VA 24061-0212, USA

D. TAYLOR
Dept. of Operative Dentistry, Dental Research Center, The University of North Carolina Chapel Hill, NC 27599-7455, USA

M. BRADEN
IRC in Biomedical Materials, The Institute of Orthopaedics, Royal National Orthopaedic Hospital, Stanmore, Middx. HA7 4LP, UK

A series of experimental soft lining materials has been produced using a butadiene/styrene copolymer with methacrylate monomers, and assessed in terms of their tensile properties. Three different methacrylate monomers, n-hexyl (HMA), ethyl hexyl (EHMA) and 1-tridecyl (TDMA), and two different initiators, benzoyl peroxide (BP) and lauryl peroxide (LP), were used. Other variables were copolymer/monomer ratio and level of cross-linking. Water sorption studies were also carried out on some of the materials, selected in terms of strength, on the pure copolymer (with and without partitioning agent) and on homopolymers of HMA and EHMA. Generally, the EHMA-based materials had the highest strengths and the TDMA the lowest. The highest tensile strength at 11.36 ± 1.80 MPa was produced by the 50/50, LP initiated EHMA material with 1% cross-linking agent, which also had the lowest water uptake. There appeared to be a relationship between tensile strength and water uptake. Water uptake was found to be governed by the partitioning agent in the copolymer powder.

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1. Introduction

Existing soft lining materials may be broadly classified into two main types, silicone rubber and soft acrylic. Most silicone rubber materials have problems with adhesion to poly(methyl methacrylate) denture base, although this has been overcome to some extent with the introduction of heat-cured, chemically modified silicones such as Molloplast B (Karl Huber GmbH & Co. KG, Germany) [1]. Soft acrylics tend to harden in the mouth due to loss of plasticizer [2]. The plasticizers used are generally phthalates, the toxicity of which has become a cause for concern [3, 4].

Possible ways of overcoming the latter problem include:

(a) use of a polymerisable plasticizer;

(b) use of a powdered elastomer with a methacrylate monomer.

In 1965 Litchfield and Wood patented a soft acrylic material containing a polymerisable plasticiser, di-2-ethyl hexyl maleate. The material proved rather rigid [5] and contained 2-ethoxyethyl methacrylate which has since proved to be biologically suspect [6, 7].

The same plasticiser was used in the development of a soft acrylic material using 1-tridecyl methacrylate monomer and a butyl/ethyl methacrylate copolymer. However, an abnormally high water uptake was noted in prolonged water absorption studies [8]. The high uptake was thought to be caused by the presence of water soluble impurities. These act as sites that attract water, forming droplets that will grow until the osmotic pressure is balanced by the elastic forces of the material. Clinical trials of this material revealed mechanical failure which, in many cases, was accompanied by blistering. Both problems were thought to

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* To whom correspondence should be sent.

be caused by the excessive water uptake. As it would be difficult to ensure that there are no water soluble impurities present, improving the strength of the material to enable it to withstand the osmotic pressure would seem to be the best option.

Work by Davy and Braden [9] on the mechanical properties of poly(alkyl methacrylate)s demonstrated that strength decreases drastically as the homologous series is ascended. 1-tridecyl methacrylate (C_{13}), used in the material described above, proved to produce the weakest polymer.

Parker and Braden [10] produced a number of experimental materials based on the use of a powdered elastomer with a methacrylate monomer. Again, mainly the higher, and hence weaker, methacrylate monomers were used. However, the best elongation to break values were obtained for a butadiene/styrene copolymer based material. Further work proved the material to have good tear resistance but high water uptake [11].

The object of this study was to formulate materials of improved strength and reduced water uptake using a butadiene/styrene copolymer.

2. Materials and methods

2.1. Materials

The materials used are listed in Table I. The initiator was dissolved in the monomer component, and the resulting liquid mixed with the copolymer and left to gel. The formulations tested are listed in Table II.

2.2. Preparation of specimens

1 mm thick sheets of the materials were produced by wet curing the gels in a metal mould. The curing cycle was slow heating in water up to 100 °C over approximately 30 min and then maintaining at 100 °C for another 30 min.

Sheets of pure elastomer were prepared by casting from a solution of the elastomer in chloroform. To produce a sheet of elastomer without partitioning agent, the solution was first centrifuged to remove the partitioning agent. To ensure that it had all been removed an ash test was carried out, producing no residue.

Sheets of the homopolymers of HMA and EHMA were produced by heat-curing the relevant monomer in a pressure cooker between glass slides using a rubber spacer; the formulations were equivalent to the monomer mixes of BS2 and BS4.1 given in Table II.

2.3. Tensile tests

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 six specimens of each formulation were tested. A 20 mm length of the central section of each specimen was marked with reflective spots. This was to enable the extension to be monitored continuously. Specimens were tested in a J&J Instruments tensile testing machine at a machine speed of 500 mm/min. Extension was measured using an infrared extensometer attachment. Maximum load and extension at break were recorded and used to calculate ultimate tensile strength and percentage elongation at break.

TABLE I Materials

Code	Material	Supplier
BS	70/30 block copolymer butadiene styrene.	Plasocoats systems Ltd
HMA	n-hexyl methacrylate.	Rhoem GmbH
EHMA	2-ethyl hexyl methacrylate.	ICI Chemicals
TDMA	1-tri decyl methacrylate.	Rhoem GmbH
BP	benzoyl peroxide (Lucidol), 50/50 mix with dicyclohexyl phthalate.	AKZO Chemicals Ltd
LP	lauryl peroxide.	BDH Chemicals Ltd

TABLE II Formulations and their codes

Code	Monomer	Initiator		EGDM
BS1	HMA	BP	1	0.5
BS2	HMA	LP	1	0.5
BS3	EHMA	BP	1	0.5
BS3.1	EHMA	BP	1	1
BS3.2	EHMA	BP	1	2
BS3.3	EHMA	BP	1	5
BS3.4	EHMA	BP	2	2
BS4	EHMA	LP	1	0.5
BS4.1	EHMA	LP	1	1
BS5	TDMA	BP	1	0.5
BS5.1	TDMA	BP	1	1
BS6	TDMA	LP	1	0.5
BS6.1	TDMA	LP	1	1

2.4. Water absorption

Water absorption characteristics of materials BS1, BS2, BS3, BS4, BS4.1 the pure elastomer (with and without partitioning agent) and the homopolymers of HMA and EHMA were assessed using specimens approximately 20 × 40 × 1 mm 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 formulation 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 percentage weight change against square root time in minutes for both absorption and desorption. Solubility was calculated as the difference between initial dried weight and minimum desorbed weight as a percentage of initial dried weight.

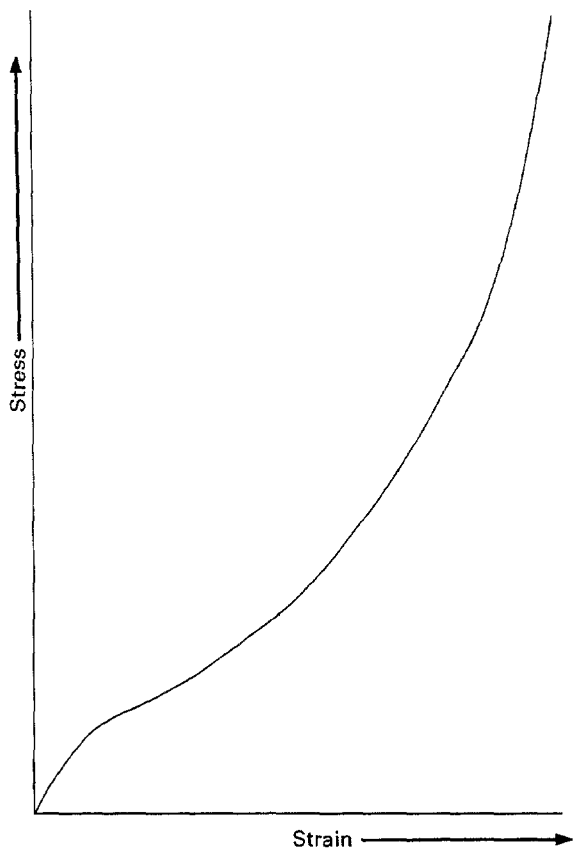

Figure 1 Typical stress/strain curve.

3. Results

3.1. Tensile test

Fig. 1 shows a typical stress/strain curve of the materials tested. Table III gives ultimate tensile strength and elongation to break for all the formulations tested. Fig. 2 compares the results for the 50/50 and 60/40 materials. Fig. 3 compares the results for the three monomer systems with the two different initiators. Fig. 4 shows the results for the HMA and EHMA systems with various levels of cross-linking and initiator.

3.2. Water absorption

Fig. 5 shows plots of percentage weight increase against square root time for the first absorptions of the tested formulations. Fig. 6 shows the absorption plots for the pure elastomer (with and without partitioning agent) and Fig. 7 those for the homopolymers of HMA and EHMA. Fig. 8 shows the desorption plots for all the formulations tested and Fig. 9 a comparison of first and second sorptions of BS1 and BS2, Fig. 10 those of BS3, BS4 and BS4.1. Table IV gives the percentage uptake at 196 days for the first sorption and solubility as a percentage of the initial dried weight.

4. Discussion

4.1. Tensile test

Fig. 1 shows a typical stress/strain curve for the higher strength materials; its profile is typical of elastomers with the characteristic upturn as fracture stress is approached. Tensile strength and elongation at break data for all the materials tested is given in Table III. As was expected the TDM based materials (BS5, BS5.1, BS6 and BS6.1) produced the lowest tensile strength.

Fig. 2 compares the effect of elastomer/monomer ratio on the ultimate tensile strength. Those materials containing lauryl peroxide as initiator, (BS2 BS4 and BS6), show no significant differences in strength between the two ratios. Those materials containing benzoyl peroxide, (BS1, BS3 and BS5) do show a noticeable difference in strength for all three monomers, the lower elastomer materials having the higher strengths. It is interesting that the strengths of all three 60/40 materials had similar strengths at around 1 MPa. It is proposed that a form of phase inversion occurs between the two ratios similar to that found by Parker and Braden for a natural rubber/nonyl methacrylate system [10]. The same effect is not seen with the lauryl peroxide initiated materials, probably due to differences in the rate of polymerisation between the two initiators. As the 60/40 gels were generally

TABLE III UTS and elongations for all formulations

Code	50 Polymer/50 Monomer				60 Polymer/40 Monomer			
	UTS (MPa)	± SD	Elongation (%)	± SD	UTS (MPa)	± SD	Elongation (%)	± SD
BS1	7.86	1.38	543.55	39.42	1.10	0.09	515.08	15.47
BS2	7.11	1.78	473.73	52.74	8.66	0.19	586.80	19.81
BS3	3.67	1.64	420.46	35.64	1.07	0.08	326.25	14.39
BS3.1	7.81	1.44	381.45	25.94	x	x	x	x
BS3.2	3.96	0.23	359.90	20.73	x	x	x	x
BS3.3	4.62	0.46	310.00	40.51	x	x	x	x
BS3.4	9.90	1.91	360.00	35.70	x	x	x	x
BS4	9.47	1.54	437.75	27.40	7.29	1.31	517.92	52.06
BS4.1	11.36	1.80	473.90	45.31	x	x	x	x
BS5	3.17	1.67	405.63	45.03	0.98	0.09	444.57	41.75
BS5.1	1.69	0.33	431.50	45.80	x	x	x	x
BS6	4.63	1.03	334.41	55.21	4.31	0.73	472.93	57.65
BS6.1	4.49	0.82	344.10	33.20	x	x	x	x

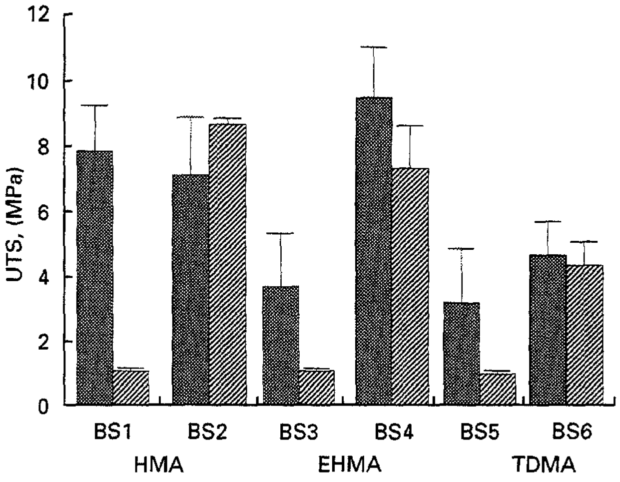

Figure 2 Tensile strength of 50/50 (▨) and 60/40 (■) materials.

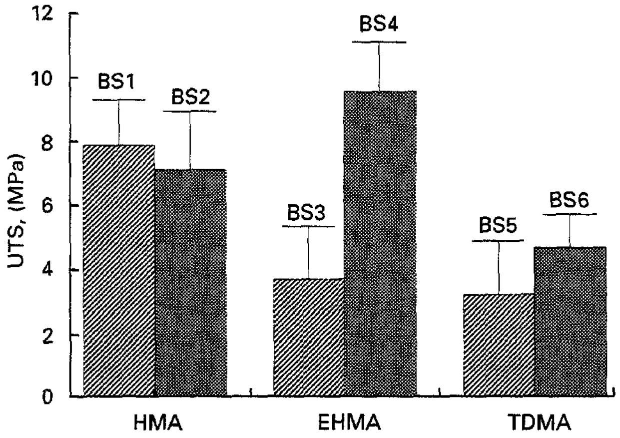

Figure 3 Tensile strength of BS1, 2, 3, 4, 5 and 6 (▨ benzol peroxide; ■ lauryl peroxide).

more viscous and difficult to handle it was decided to restrict further work to using only 50/50 formulations.

Fig. 3 compares the effect on strength of the two initiators. Only the EHMA material showed any significant difference, the LP initiated having the highest strength. Lauryl peroxide is the preferred initiator in that it does not produce water soluble by-products. Using benzoyl peroxide results in the production of benzoic acid which is soluble at 37 °C.

The effect of varying levels of cross-linking and initiator on the strength of the EHMA based system can be seen in Fig. 4. The findings of earlier work [11] using tear energy measurements to assess the formulations concluded that optimum level of EGDM was 1% for EHMA, BP initiated materials. This agrees with the present results where increasing the EGDM content from 0.5% to 1% (BS3 and BS3.1) doubles the tensile strength. A further increase in level to 2% (BS3.2) reduces the strength and even with an increase to 5% EGDM(BS3.3) the strength remains at the same level. However, the combination of an increase of BP to 1% and an EGDM level of 2% gives the highest strength of all the BP initiated materials. With the LP initiated materials, use of 1% EGDM produces a slight increase in strength.

The material with the highest tensile strength is BS4.1, the LP initiated 50/50 EHMA material with 1% EGDM.

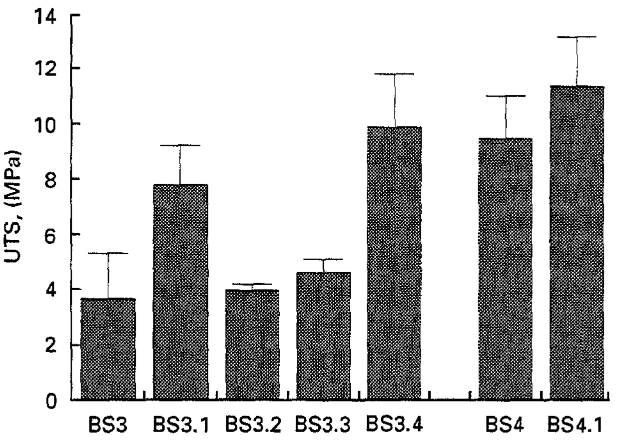

Figure 4 Tensile strength of BS3, 3.1, 3.2, 3.3, 3.4, 4 and 4.1.

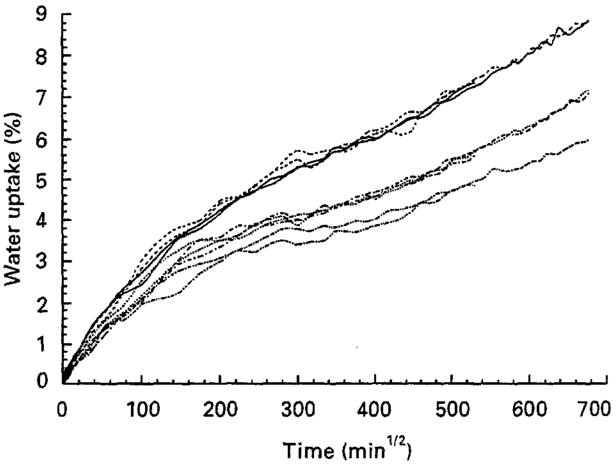

Figure 5 Plot of percentage water uptake as a function of time$^{1/2}$ for the first sorption of BS1 (—), 2 (- - -), 3.1 (.....) 4 (– – –) and 4.1. (- - - - - -).

4.2. Water absorption

The materials to be assessed were selected in terms of strength. For the first absorption none of the formulations tested reached equilibrium during the time-scale of the investigation (~ 10 months). Fig. 5 shows the materials to have uptakes in the range 6–9% and still rising. The EHMA based materials (BS3.1, BS4 and BS4.1) have lower uptake than those based on HMA (BS1 and BS2) with BS4.1 having the lowest uptake.

The source of the high uptake of these materials is thought to be the partitioning agent, a necessary additive to the powdered elastomer to prevent agglomeration on storage. This partitioning agent is likely to be talc and so is soluble. In water, this will give rise to the formation of solution droplets at the sites of the partitioning agent. The droplets will then grow, the driving force being the chemical potential gradient between the droplet and the external solution. Obviously, the modulus of the material will influence the extent to which the droplet grows. BS4.1 has the highest tensile strength and the lowest rate of uptake.

That the high water uptake is caused by the presence of the partitioning agent is supported by the absorption results for the pure elastomer in Fig. 6. The uptake for the elastomer with partitioning agent is

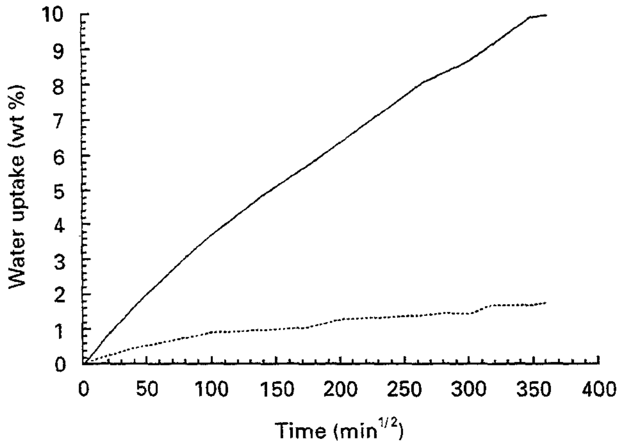

Figure 6 Plot of percentage water uptake as a function of time$^{1/2}$ for the pure elastomer with (—) and without (---) partitoning agent.

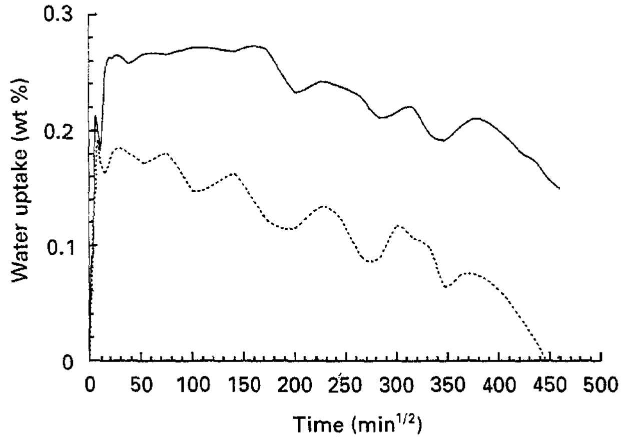

Figure 7 Plot of percentage water uptake as a function of time$^{1/2}$ for the HMA (—) and EHMA (----) homopolymers.

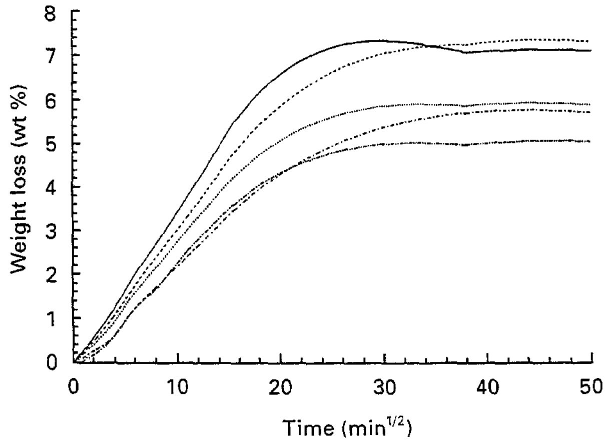

Figure 8 Plot of percentage weight loss as a function of time$^{1/2}$ for desorption of BS1 (—), 2 (---), 3.1 (····), 4 (----), 4.1 (---).

over 6% after only 4 weeks and is still rising. In the same time period the elastomer without the partitioning agent is about 1%. Furthermore, the uptake of the homopolymers of HMA and EHMA (Fig. 7) is also very low and would not contribute to the high uptake of the formulations tested.

TABLE IV Water uptake data – first uptake and solubilities

Code	Water uptake (wt%)	Solubility (wt%)	Total uptake (wt%)
BS1	7.33	0.25	7.58
BS2	7.39	0.31	7.70
BS3.1	5.71	0.45	6.16
BS4	5.58	0.39	5.97
BS4.1	4.84	0.38	5.22

Removed from water at 196 days

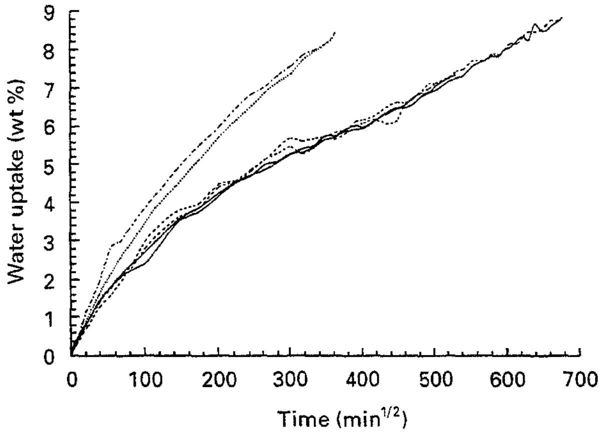

Figure 9 Plot of percentage water uptake as a function of time$^{1/2}$ for first and second sorption of BS1 and BS2 (BS1-1—; BS2-2----; BS2-1 ---; BS2-2····).

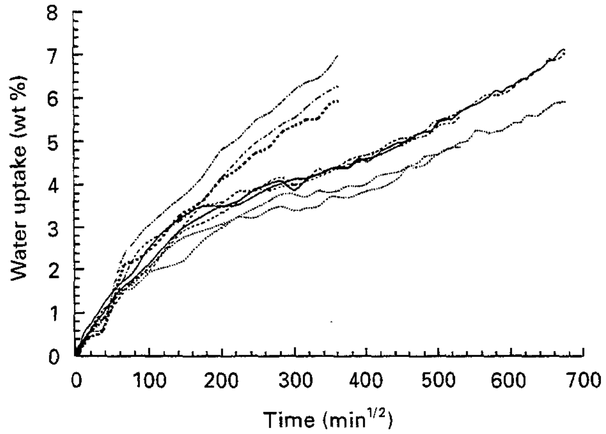

Figure 10 Plot of percentage water uptake as a function of time$^{1/2}$ for first and second sorptions of BS3.1, 4, and 4.1 (BS3.1-1—; BS3.1-2 ----; BS4-1 ---; BS4-2 -----; BS4.1-1 ····; BS4.1-2 ---).

Desorption of all materials (Fig. 8) was rapid, equilibrium being attained within 24 h, and appears to conform to classical diffusion theory. This is in accord with the findings of Muniandy and Thomas [12] for natural rubber. Calculation of a diffusion coefficient would give misleading results as the materials were not at equilibrium when removed from water for desorption. Table IV gives percentage weight increase, solubility and actual water uptake at 196 days. Solubility of all the materials is low and of the same order. It is attributed to loss of residual monomer and low molecular weight material and leaching of any soluble material.

Second absorption data for the HMA materials BS1 and BS2 is shown in Fig. 9. For both materials the second absorption is faster and higher. The second absorption data for the EHMA materials (Fig. 10) similarly shows the second uptake higher than the first. During the first absorption the swelling of the droplets may have caused permanent deformation to the material. As a result of this deformation the droplets will swell more quickly in the second absorption giving a higher uptake. In the first sorption the uptake of BS3.1 and that of BS4 were similar, in the second absorption that of BS3.1 is higher. This indicates that the deformation or damage caused by the first absorption was more severe for BS3.1 than BS4 so allowing faster uptake for the second absorption. The uptake in the second absorption of the EHMA-based materials can be linked to their tensile properties, the higher the strength the lower the water uptake.

5. Conclusions

The highest strength material comprised a 50/50 wt/vol mix of the copolymer with ethyl hexyl methacrylate containing 1% ethylene glycol dimethacrylate and 1% lauryl peroxide. This formulation also had the lowest water uptake.

There appeared to be a correlation between tensile strength and water uptake of the ethyl hexyl methacrylate based materials.

The relatively high water uptake of these butadiene/styrene based materials can be attributed to the presence of a partitioning agent.

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