ULTRASONICALLY SET GLASS POLYALKENOATE CEMENTS FOR ORTHODONTIC APPLICATIONS.

D.A. Tanner, N. Rushe & M.R. Towler*

Materials & Surface Science Institute, University of Limerick, National Technological Park, Limerick, IRELAND.

* Address for Correspondence

Dr Mark Towler,
Research Scholar,
Materials and Surface Science Institute,
University of Limerick,
Technological Park,
Limerick,
IRELAND

Tel.. +35361 213055
Fax.. +35361 213529
Email.. Mark.Towler@ul.ie

Keywords: Glass Polyalkenoate Cements, Ultrasound, Luting Cements

ABSTRACT

There is an accepted clinical requirement for a luting cement that can be command set upon satisfactory placement of an orthodontic appliance onto dentition. This work evaluates the suitability of ultrasound, imparted from a dental scaler, as a potential mechanism for achieving this. The net setting times and subsequent compressive strengths of a range of commercial and experimental glass polyalkenoate cements (GPCs) were evaluated, using modified ISO 9917 methods, when set both chemically and by ultrasound. The ultrasound was applied to the GPC through an orthodontic brace. It was possible to command set GPCs by the application of five to ten seconds of ultrasound; the exact time required being dependent upon the composition of the GPC in question. The compressive strengths of these cements can be improved by around 90% with the command set when the optimum PAA molecular weight and tartaric acid content is employed.

1. INTRODUCTION

Glass polyalkenoate cements (GPCs) were developed in the 1960's [1] and are now used in dentistry as both luting and restorative cements. GPCs are formed by the reaction of an ion leachable alumino-silicate glass with an aqueous solution of poly (alkenoic acid), PAA. Water is used as the reaction medium [1]. A two-stage setting reaction occurs, resulting in a cement of residual glass particles embedded in a hydrogel polysalt matrix [2]. During the first setting stage the material is susceptible to water uptake and during the second it is susceptible to dehydration [3]. This relationship with water has traditionally limited the use of GPCs in orthodontic and restorative dentistry. In an attempt to address this problem, resin modified GPCs (RMGPCs) were developed. These are similar materials to conventional GPCs [4] but contain a photo-polymerisable monomer [5] which initiates a command set upon the application of an intense light source. However, they have significant disadvantages inherently related to the presence of the resin, in that they swell in aqueous media [6], they have poor long-term mechanical properties [7, 8] and there are toxicological concerns with micro-leakage of the monomer [9]. There is also a logistical problem in transmitting light through a brace or bracket to initiate polymerisation, meaning that RMGPCs have limited applicability in orthodontics. An alternative method of command set which does not require the incorporation of additional chemicals, or the need to transmit light through solid materials, would be a major breakthrough in the orthodontic field.

Some of the factors that influence the setting, and subsequently the mechanical properties, of GPCs are listed below:

1. *Particle Size,* The setting regime and subsequent mechanical properties of GPCs are influenced by the particle size and particle size distribution of the glass. The particle size of the glass in luting GPCs is small compared to restorative GPCs and hence the specific surface area is increased, providing a greater surface area for acid attack, thereby reducing setting time.
2. *Addition of Tartaric Acid (TA).* Optically activated TA is a cement-former in its own right, but its cements are unstable toward water [10]. However,

when added in moderate amounts to GPC systems, TA can increase working time and sharpen the set [11]. TA forms strong complexes with aluminium, thereby enhancing the extraction of aluminium from the glass [12]. Initially, TA alone complexes cations but then as neutralization proceeds (with pH rising to 3), PAA becomes neutralized by metal ions until the cement sets (around pH 5). Additionally, the ionization of PAA is suppressed and the unwinding of its chains is retarded, thus reducing the viscosity of the paste and delaying gelation. However, once gelation occurs, TA accelerates hardening. Since TA and calcium react preferentially, the initial set may be due to the formation of calcium tartrate [13].

3. *The molecular weight of* polyacrylic acid *(PAA).* High molecular weight PAA increases the viscosity of unset GPC and reduces the setting time but also leads to an increase in mechanical properties [14-16].

4. *Ultrasonic Setting (US).* The effects of ultrasound derive from acoustic cavitation; the formation, growth and collapse of bubbles producing intense local heating [17]. In liquid/solid slurries such as GPCs, bubble collapse launches shock waves into the liquid and when these pass over particles in close proximity to one another, high velocity collisions occur. If the collision is at a direct angle, powder particles can be driven together to induce melting at the point of collision, resulting in particle agglomeration. If the particles collide at a glancing angle, a mechanical removal of surface material results in particles being further broken down [18]. Ultrasound is routinely used for setting cement in the building industry and the authors have previously shown that restorative GPCs can be command set by a similar process, where ultrasound is imparted from a dental scaler [19-21]. All previous research by the authors was performed on high viscosity restorative GPCs. For these cements, the application of ultrasound reduced porosity and improved glass particle packing on re-orientation [22] thereby imparting a command set and superior mechanical properties to the GPC, particularly within the first 24 hours after setting. Additional literature confirms the suitability of ultrasound for improving the mechanical properties of restorative GPCs [23]. USGPCs do not

require monomer incorporation and therefore avoid the drawbacks associated with RMGPCs.

To date, there have been no studies looking at the ultrasonic setting of luting GPCs. These tend to be more fluid than restorative GPCs and contain particles of smaller size to assist in the production of low film thicknesses. It is accepted that the motion taken up by a particle in the ultrasound field will depend upon the relationship between the particle's size and mass and the fluidity of the matrix [18, 24]. Small light particles will move with a fluid matrix, whereas large dense ones will not. Intermediate particles will move with an amplitude dependent upon their size and mass. Conversely, the ease of particle movement, hence the likelihood of particles coalescing ~~(if they are friable solids will then not be more likely to break up?) – yeah once they've set but we are talking about the process of setting~~, will depend upon matrix fluidity.

The objective of this work is to evaluate the handling and mechanical properties of a selection of commercial and experimental luting GPCs when allowed to set both chemically and by ultrasound. The influence of PAA molecular weight and TA content on the properties of the experimental GPCs will be evaluated with respect to setting regime after one and seven days maturation. Standard ISO tests for setting time and compressive strength evaluation have been modified to more closely reflect the clinical situation.

2. METHODS

2.1 Materials

The following luting GPCs were assessed:

- Ketac Cem Radiopaque (KC); Batch #165450 (ESPE, Germany).
- Fuji I (FI); Batch #0306041 (GC, Japan).
- Experimental GPC. This cement was based on $4.5SiO_2 3Al_2O_3 1.5P_2O_5 3SrO 2CaF_2$ glass mixed with three different PAAs; E7, E8 and E9 (Advanced Healthcare Limited, Kent, UK). The molecular weights of the PAAs are included in table 1. TA was incorporated in 10wt% and 20wt% amounts in order to evaluate its effect on handling properties and resultant compressive strengths. The powder:acid:liquid (P:A:L) mixing ratio (glass:acid:water/TA solution) used was 9:2:4; designed to mimic the handling properties of the commercial GPCs.

Table 1: Here

All the GPCs were hand mixed with a spatula on a glass slab. Mixing of the commercial GPCs took place in accordance with the directions supplied by the manufacturers. The ultrasonic equipment employed was a Piezon® Master 400 dental scaler (EMS, Nyon, Switzerland). The insert used (DS-003) was developed for scaling applications.

2.2 Working and Setting Times

The working and net setting times of the cements were evaluated when the GPCs were left to set both chemically (CS) and ultrasonically (US). The standard ISO test method to evaluate net setting time [25] was modified by reducing the amount of GPC tested from $400mm^3$ to around $40mm^3$ to more closely reflect the clinical situation. Evaluation of chemical net setting time was otherwise in line with ISO 9917. To evaluate the setting time ultrasonically, a metal orthodontic bracket was secured to the end of the ultrasonic tip. A thin layer of cocoa butter was applied to the bracket to prevent adhesion to the unset GPC. Curing was undertaken by transference of ultrasound from the tip, through the bracket and onto the GPC for five second

durations. The ISO setting needle was then applied to the surface of the GPC after each application to determine whether setting has occurred.

2.3 Compressive Testing

The compressive strengths of the cements were evaluated by standard ISO test methods [25] after 1 and 7 days. However, the samples prepared were reduced in size (3mmØ x 4mm height) to more closely mimic the clinical situation. Otherwise, preparation was in line with ISO 9917. Ten samples of each GPC were produced and five were set by conventional chemical (CS) means. The remaining five were set ultrasonically (US). All GPCs were then left in the moulds (37±2°C) for one hour, subsequently demoulded and stored in distilled water (37±2°C) prior to testing. An Instron Tensometer (Instron Ltd., High Wycombe, UK) was employed for the test at a crosshead displacement rate of 1mm min^{-1}. The compressive strength, σ_c, was calculated according to:

$$\sigma_c = 4F/\pi d^2 \quad (1)$$

where:

F= maximum load applied (N)

d= test piece diameter (m)

RESULTS AND DISCUSSION

The working and net setting times of KC, set chemically, were 190s and 210s, respectively. The working and ISO setting times of FI, set chemically, were 210s and 200s, respectively. These results are compiled in table 2. With the application of US the setting time for both cement systems is reduced and full command setting was achieved with 5 seconds of ultrasonic exposure.

The compressive strengths of the commercial GPCs were evaluated when set by both CS and US. The results are shown in table 3. The mean compressive strengths of KC and FI after 1 day were 127MPa and 129MPa, respectively. Ultrasonic exposure had little effect on the mean strengths of the KC and FI cements (130MPa and 128MPa, respectively). Compressive testing was repeated on samples matured for 7 days and the strengths were found to increase to 136MPa for KC when set by both methods and to 144MPa for FI for both methods. There is no statistical difference in recorded compressive strengths between the commercial samples at either time duration when set by either technique. Thus, whilst the ultrasound command sets the commercial GPCs, it does not appear to improve the mechanical properties. This is in disagreement with the increases from ultrasound found for restorative versions of these cements, Ketac Molar Quick (KMQ, ESPE, Germany) and Fuji IX Fast (FIXF, GC, Japan) [21]. The reason for this is not clear but is likely to be related to the higher fluidity and lower particle sizes of the luting GPCs.

Table 4 shows the working and setting times of the experimental GPCs and their variation with PAA molecular weight, TA content and maturation time. Many commercial GPCs contain 10wt% TA, incorporated to extend working time, whilst maintaining an acceptable set. The effect of incorporating two different quantities of TA (10wt% and 20wt%) on both the handling and compressive strengths of the experimental GPCs was evaluated. Figures 1 and 2 show the working and net setting times of the experimental GPCs, which varied depending upon PAA molecular weight and the presence of ultrasound. The experimental GPCs could not be command set with the application of 5s US. However, all GPCs could be set by the application of 10s US, implying that the experimental GPCs do not respond to US as well as their commercial counterparts.

The experimental GPCs containing 10wt% TA have similar working and setting times to the two commercial materials. However, whilst the addition of further TA (to 20wt%) extends the working time as expected, the setting time is not sharpened; rather it is extended. For the GPCs containing low molecular weight PAA, the setting time extends to over 17 minutes, suggesting that additional TA will not produce suitable cements for orthodontics. However, although none of the experimental materials, regardless of TA content, will set by the application of 5s US, they all set by the application of 10s US (results included in table 5 and figures 3 and 4) and whilst the compressive strengths of these GPCs are all lower than their commercial counterparts, increases in strength resulting from a combination of increased TA content and ultrasonic setting suggest such materials may have potential in orthodontics. There is an increase in strength, as expected, with maturation time. Although the addition of 20wt% TA results in a much slower set, the resultant strengths are improved by the addition of increased TA, suggesting that when setting does commence, it occurs very rapidly resulting in higher strength. The use of high molecular weight PAAs would expect to result in better strengths [15, 16] but the results do not bear this out. The GPCs exhibit their poorest strengths when mixed with the highest molecular weight PAA (E9), regardless of maturation time, TA content and mode of set. This is likely to be due to the difficulties in hand mixing GPCs based on high molecular weight PAAs. The GPCs based on the high molecular weight PAA also follow the same trends when set by ultrasound. This is likely to be due to a combination of the problems with mixing and also with the lack of fluidity of the matrix [24] inhibiting the movement of the small glass particles from coalescing into a cohesive body. The best compressive strengths are recorded by GPCs based on E8 PAA, particularly when mixed with 20wt% TA and set ultrasonically. The E8/20wt%TA, ultrasonically set GPC shows a major increase in compressive strength (95%, 1 day) and (70%, 7 days) over the chemically set, 10wt% TA GPC based upon the same acid.

CONCLUSION

The work has shown that ultrasound can be imparted through an orthodontic bracket to command set GPCs. This is likely to be due to a combination of cavitation, improved mixing of the constituents and better compaction. Cavitation has previously been observed in GPCs where mean particle size was reduced after ultrasonic application [20] indicating that collisions between particles are occurring.

Application of ultrasound has resulted in both a command set and an improvement in the resultant mechanical properties. However, the extent of that improvement is also dependent upon the cement composition. The incorporation of 20wt%TA results in a GPC that sets too slowly for conventional use. However, when this cement is set by ultrasound the GPC has a command set and much improved strength. Such a method of setting which does not require the incorporation of additional chemicals, or the need to transmit light through solid materials, could be a major breakthrough in the orthodontic field. Such materials could have great commercial benefit if the presence of additional TA could produce a very slow setting GPC that can be manipulated until the surgeon is satisfied with placement. At which point US can be applied, through the brackets, to command set the cement and hold the orthodontic appliance firmly in place.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of the Enterprise Ireland Technology Development Program ('Proof of Concept' phase, PoC/2003/018).

REFERENCES

1. BE. KENT and AD. WILSON, *Br Dent J*. **135** (1973) 322.
2. S. CRISP and AD. WILSON, *J Dent Res.* **53** (1974) 1408.
3. RJG. DE MOOR and RMH. VERBEECK, *Biomaterials.* **19** (1998) 2269.
4. SB. MITRA *J Dent Res;* **70** (1991) 72-74
5. SB. MITRA, *European Patent Application.* No. 0323 120 **A2**; (1989)
6. P SASANALUCKET, KR ALBUSTANY, PJ DOHERTY and DF WILLIAMS, *Biomaterials,* **14** (1993) 906-916.
7. JW NICHOLSON and HM. ANSTICE, *J Mater Sci: Mater Med*. **3** (1992) 447.
8. W. KANCHANAVASITA, HM ANSTICE AND GJ PEARSON, J Dent **26/8** (1998) 707-712.
9. MA. CATTANI-LORENTE, V. DUPUIS, J. PAYAN, F. MOYA, and JM. MEYER, *Dental Materials*. **15/1** (1999) 71.
10. S CRISP and AD WILSON, J.Dent.Res. **55** (1976) 1023-1031
11. AD. WILSON, S. CRISP, and AJ FERNER, J.Dent. Res.**55** (1976) 489-495
12. HJ PROSSER, SM JEROME and AD WILSON, J.Dent.Res. **61** (1982) 1195-1198
13. S CRISP, BG LEWIS and AD WILSON, J. Dent. **4** (1976) 162-166
14. R.G. HILL, C.P. WARRENS and A.D. WILSON *J. Mater. Sci.* **24** (1989) 363
15. R.G. HILL and S.A. LABOK *J. Mater. Sci.* **27** (1992). 67
16. R.G. HILL *J. Mater. Sci*. **28** (1993) 3851-58
17. K. S. SUSLICK and G. J. PRICE. *Annu. Rev. Mater. Sci. **29*** (1999) 295-326.
18. S. J. DOKTYCZ and K. S. SUSLICK. *Science **247*** (1990) 1067-1069.
19. MR. TOWLER, AJ. BUSHBY, RW. BILLINGTON and RG. HILL, *Biomaterials*. **22/11** (2001) 1401-1406.
20. MR. TOWLER, CM. CROWLEY and RG. HILL, *J. Mat. Sci.: Letters.* **22/7** (2003) 539-541.
21. E. TWOMEY, M.R. TOWLER, C.M. CROWLEY, J. DOYLE and S. HAMPSHIRE; *J. Mat. Sci.* **39/14** (2004) 4631-4632
22. SC. LEA, GJ. PRICE and AD WALMSLEY, *Ultrasonics Sonochemistry*. In Press (2003)
23. CJ. KLEVERLAAN, RNB VAN DUINEN and AJ FEILZER, *Dent Mat*. **20** (2004) 45-50.
24. GL GOOBERMAN, 'Ultrasonics: Theory and Application', English University Press, (1968)
25. ISO 9917(E) International Standard. (1991) 1-13.

Formatted: Bullets and Numbering

Formatted: Bullets and Numbering

Formatted: Bullets and Numbering

Formatted: Bullets and Numbering

Table 1: Molar mass details of the poly(acrylic) acids

CODE	Mw	Mn	PD
E7	25,700	8,140	3.2
E8	51,900	21,900	2.4
E9	80,800	26,100	3.1

Table 2: Working and setting times of commercial GPCs.

GPC	Working Time (s)	Net Setting Time CS (s)	Net Setting Time US (s)
Ketac Cem	190	210	5
Fuji I	210	200	5

Table 3: Compressive strengths of commercial GPCs

GPC	Compressive Strength CS (MPa)		Compressive Strength US (MPa)	
	1 day	7 days	1 day	7 days
Ketac Cem	127 *(11)*	136 *(22)*	130 *(10)*	136 *(7)*
Fuji I	129 *(6)*	144 *(14)*	128 *(15)*	144 *(12)*

() = standard deviation

Table 4: Working and setting times of experimental GPCs.

	Working Time (s)		Net Setting Time CS (s)		Net Setting Time US (s)	
Acid	10% TA	20% TA	10% TA	20% TA	10% TA	20% TA
E7	160	180	400	1030	10s	10s
E8	250	280	380	760	10s	10s
E9	100	180	400	580	10s	10s

Table 5: Compressive strengths of experimental GPC's

	Compressive Strength CS (MPa)				Compressive Strength US (MPa)			
Acid	10% TA		20% TA		10% TA		20% TA	
	1 day	7 days	1 day	7 days	1 day	7 days	1 day	7 days
E7	47 *(3)*	66 *(5)*	74 *(3)*	86 *(5)*	71 *(7)*	89 *(9)*	92 *(6)*	91 *(5)*
E8	45 *(4)*	55 *(3)*	68 *(4)*	84 *(3)*	62 *(9)*	63 *(6)*	88 *(3)*	94 *(10)*
E9	37 *(2)*	51 *(4)*	54 *(3)*	59 *(2)*	50 *(4)*	61 *(9)*	82 *(5)*	68 *(8)*

() = standard deviation

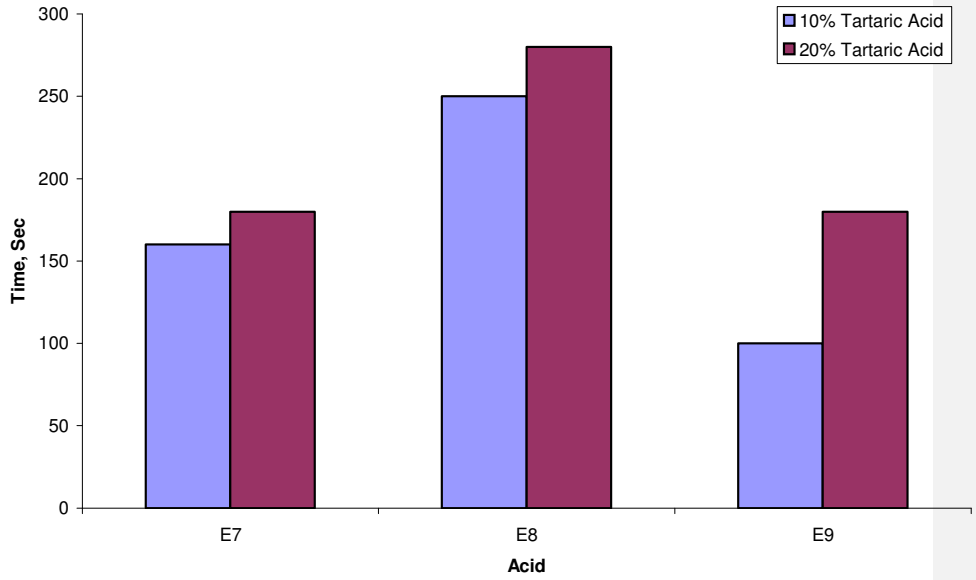

Figure 1: Working times of experimental GPCs

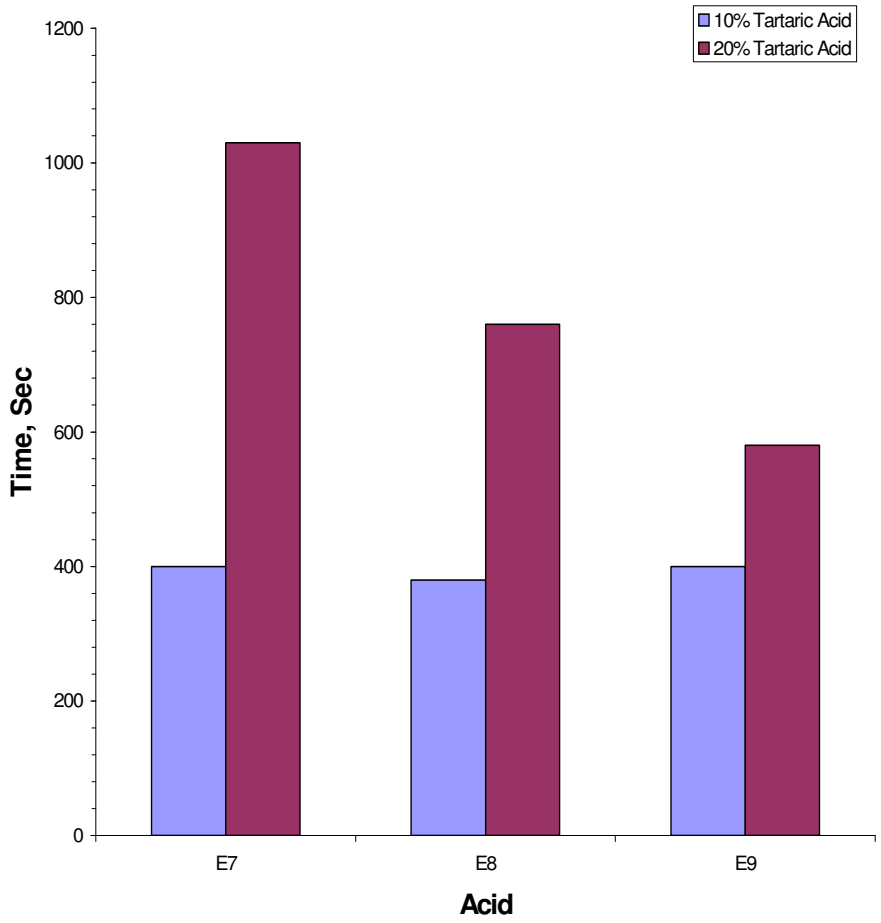

Figure 2: chemical net setting times for experimental GPCs.

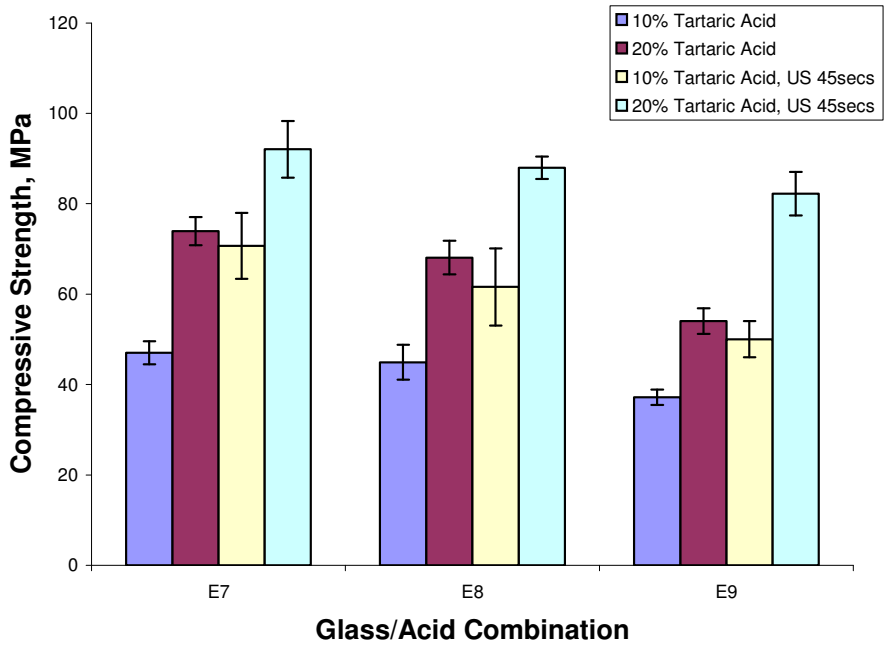

Figure 3: Compressive strengths of experimental GPCs after 1 day with 10 & 20wt% TA.

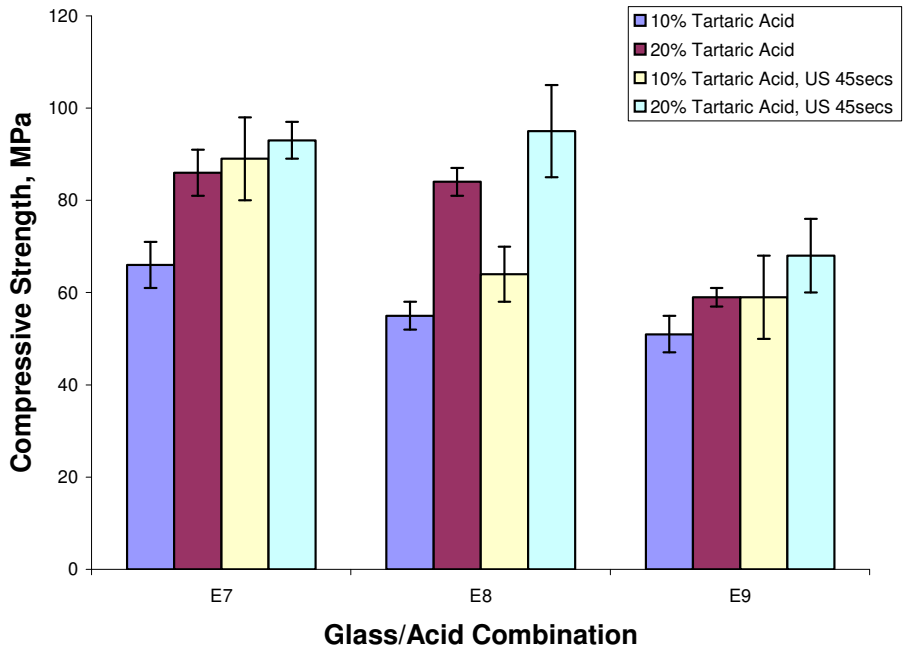

Figure 4: Compressive strengths of experimental GPCs after 7 days with 10 & 20wt% TA.