

Effect of polyacid on the properties of polyalkenoate cements

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Four polyacids were prepared by reacting acrylic acid with itaconic and maleic acids at different ratios and these were treated with a fluoroalumino calcium silicate glass to form polyalkenoate cements. The effect of working and setting times of the glass ionomer upon variation of the polyacid content in the liquid has been studied. Mechanical properties such as compressive strength and diametral tensile strength were found to increase sharply upon increase in polyacid concentration. The monomer ratio in the polyacid was also found to be critical in determining the final properties of the dental material.

GLASS ionomer cements or polyalkenoate cements as they are well known, used as dental materials were first reported by Wilson and Kent¹. These cements represented the initial step towards the ideal dental material. They are superior to other materials available especially because of their adhesive nature to both enamel and dentine and are the least irritant of cements. They have been widely used as restorative, luting and sealing materials in dentistry. Currently these materials are being imported into this country and the following work details attempt to develop this material indigenously for the first time.

The physical properties of polyalkenoate cements or glass ionomer cements depend on a number of variables such as powder:liquid ratio, strength of polyacid solution and molecular weight of the polymer²⁻⁴. On mixing the polyalkenoic acid with fluoroalumino silicate glass, the liquid erodes the glass powder surface and the metal ions of Al³⁺, Ca²⁺, Na⁺, etc. are drawn from the powder by the hydrogen ions of carboxyl radical in the liquid along with fluoride and silicic acid. When the polyacid ionizes as the pH of the aqueous phase increases, the polymer chains unwind as the negative charge on them increases and the viscosity of the cement paste increases. The concentration of the cations increases until they condense on the polyacid chain. Desolvation occurs and insoluble salts precipitate first as a sol and subsequently as a gel which represents the initial setting reaction. The cement continues to harden as cations bind more and more to the polyacid chain and hydration reaction continues.

Normal synthesis of the polyacid yields nearly a 25–30% acid solution in water. However, previous data indicate that an optimum concentration of 30–50% polyacid content is required for commercial viability⁵. It has been found that the properties of the cement are affected considerably by the polyacid content which has been

verified in this work for four polyacids synthesized indigenously.

The four polyacids used in this study were poly(acrylic acid-co-itaconic acid 4:1), poly(acrylic acid-co-itaconic acid 2:1), poly(acrylic acid-co-maleic acid 4:1) and poly(acrylic acid-co-maleic acid 2:1). All four acids were synthesized in the laboratory using a solution polymerization technique which has been described elsewhere⁶. All the acids obtained were aqueous solutions and relatively colourless with different polyacid contents in them. The dry polyacid contents in the synthesized parent solutions were determined by eliminating the water in a measured quantity of the polyacid and by weighing the dry residual polymer (Table 1). These parent solutions were either diluted or concentrated with distilled water depending on requirements for this study. The acids were characterized using gel permeation chromatography (Waters Associates, Model 6000 A, USA with absorbance detector) and UV-spectrometry (Model 240, Shimadzu make, Japan). 5% (+) tartaric acid was added to the polyacids as a chelating agent. Molecular weight of the synthesized polyacids, determined by viscometric method using an Ubbelohde viscometer and the values obtained from the Mark-Howink equation are given in Table 1.

$$[\eta] = KM^a (100 \text{ ml/g}, 25^\circ\text{C}),$$

where $K = 1.21 \times 10^{-3}$ and $a = 0.54$ for the above system⁷.

The polyalkenoate cements were prepared by reacting polyacids with glass powders containing calcium and aluminium ions. A fluoroalumino calcium silicate glass (IG-90-2687, Industrial Corporation, PA, USA) which was obtained as a gift was used in the study. The ionomer glass particles were of 1 micron size. All other chemicals used were obtained from regular laboratory suppliers and purified before. The cements were mixed at 22°C and 50% relative humidity by spatulation on a glass block using a known powder/liquid ratio. One half of the powder was incorporated into the liquid in 15 s and the rest in the next 15 s. The total mixing time was less than 60 s in all cases.

Table 1. Viscosity average molecular weights and polyacid contents determined for four polyacid solutions synthesized by solution polymerization

Polyacid	Molecular weight (M_v)	Polyacid content (%)
Poly(acrylic acid-co-itaconic acid) 4:1	27600	42.95
Poly(acrylic acid-co-itaconic acid) 2:1	32900	35.87
Poly(acrylic acid-co-maleic acid) 4:1	22700	27.10
Poly(acrylic acid-co-maleic acid) 2:1	52600	39.24

The working and setting times were determined by mixing the glass powder and the polyacid in the ratio 1:0.5 by weight on a glass plate till it formed a dough and subsequently placing the viscous sample between the metal discs of a cycloviscograph (Cyclo-visco E, Brabender Co., Germany). The cycloviscograph consists of an oscillating disc and a shear disc with a torque-measuring device. Both discs are axially aligned. The lower disc is connected to a drive unit and oscillates with an adjustable frequency and a constant oscillating angle. The top disc follows the lower disc and the torsional angle is proportional to the shear stress. The maximum shear angle depends on the viscosity of the test sample. Temperature control is achieved by micro-processor-controlled electric heating plates for each shear disc. All tests were carried out at oral temperature 37°C. The cycloviscograph was interfaced with an IBM PC to facilitate the data processing. The torque, amplitude variation and temperature were recorded by the computer. When the amplitude of the torque variation was found constant, the machine was stopped and the working time and setting time were observed from the computer.

The compressive strength (CS) and diametral tensile strength (DTS) of cements prepared using liquids of different polyacid content were determined as follows. A split mould made of brass was used for preparing all specimens for compressive strength measurements. Specimens of sizes 3 mm diameter and 6 mm depth were moulded by packing the dough into the cavities in the mould. To obtain close packing, the sides of the mould were flattened with glass sides and tightened with C-clamps. Immediately after packing, the mould with the C-clamp was transferred into an oven maintained at 37°C for one hour. The specimens were taken out and stored for a further 24 hours at 37°C in distilled water. Subsequently, each sample was kept between the platens of a universal testing machine (INSTRON, Model 1011, UK) and load was applied continuously till a break occurred. The compressive load at break (N) was measured and the compressive strength was calculated using the formula, Load/area. Cross-head speed was kept constant at 10 mm/min for all testings.

The mould for preparing diametral tensile strength specimens was made of stainless steel having cavities 6 mm in diameter and 3 mm in depth. The mould was initially coated with a mould release silicon agent and the glass ionomer dough was then packed into the cavities. Both the sides of the cavities were then covered with glass slides and clamped with a C-clamp as before. The mould was then kept inside the oven for 1 hour at 37°C, specimens taken out and kept in distilled water for 24 hours at the same temperature. Each specimen was subsequently kept between the platens of the universal testing machine and tested for load at break at a cross-head speed of 10 mm/min. The DTS was calculated using the equation

$$DTS = 2P/3.14 DL,$$

where P is the load in Newtons, D is the diameter of the specimen in mm and L is the height of the specimen in mm.

UV spectra showed characteristic absorption maxima at 272–275 nm indicative of carbonyl group absorption and gel permeation chromatography indicated a narrow molecular weight distribution for all the polyacids studied. The viscosity measurements found the molecular weights to lie between 20,000 and 50,000 which is similar to the reported values for commercial liquid resins⁸. Three factors are expected to govern the rate of cement-forming reaction – the mass action effect of the polyacid concentration; the viscosity of the liquid (and hence the MW) and the $P:L$ ratio. It is the interplay between the three factors which governs the complex relationships between the setting time and the polyacid concentration. The factor which controls the setting may be the mass action effect. When the polyacid content becomes higher, the viscosity increases significantly and is found to retard the setting reaction.

The working times were not monitored as this is dependent only on the $P:L$ ratio which was kept constant in this case. Setting times did not show considerable

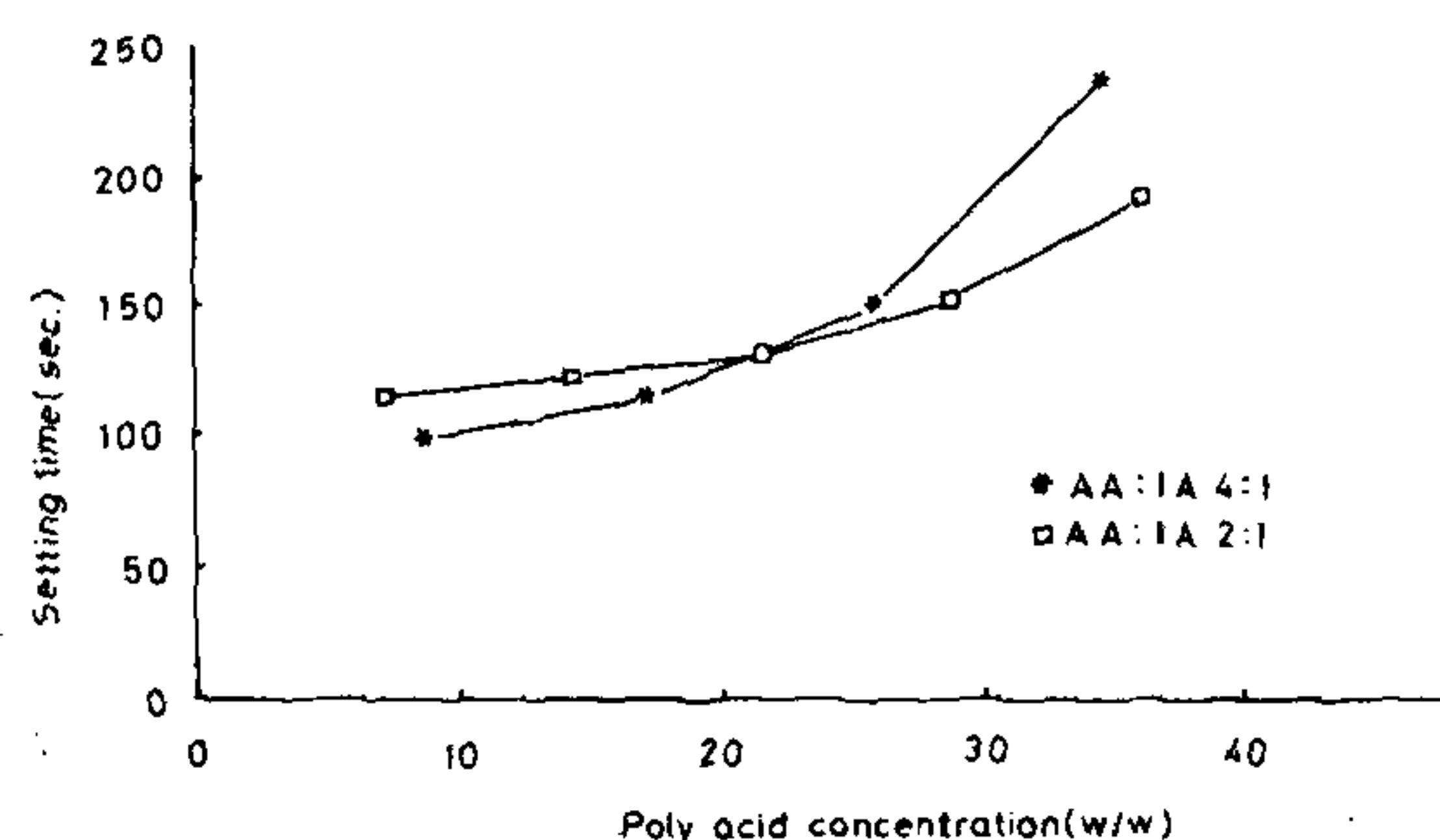


Figure 1. Effect of polyacid content on the setting time of poly(acrylic acid-co-itaconic acid 4:1) [*] and poly(acrylic acid-co-itaconic acid 2:1) [□] when reacted with glass.

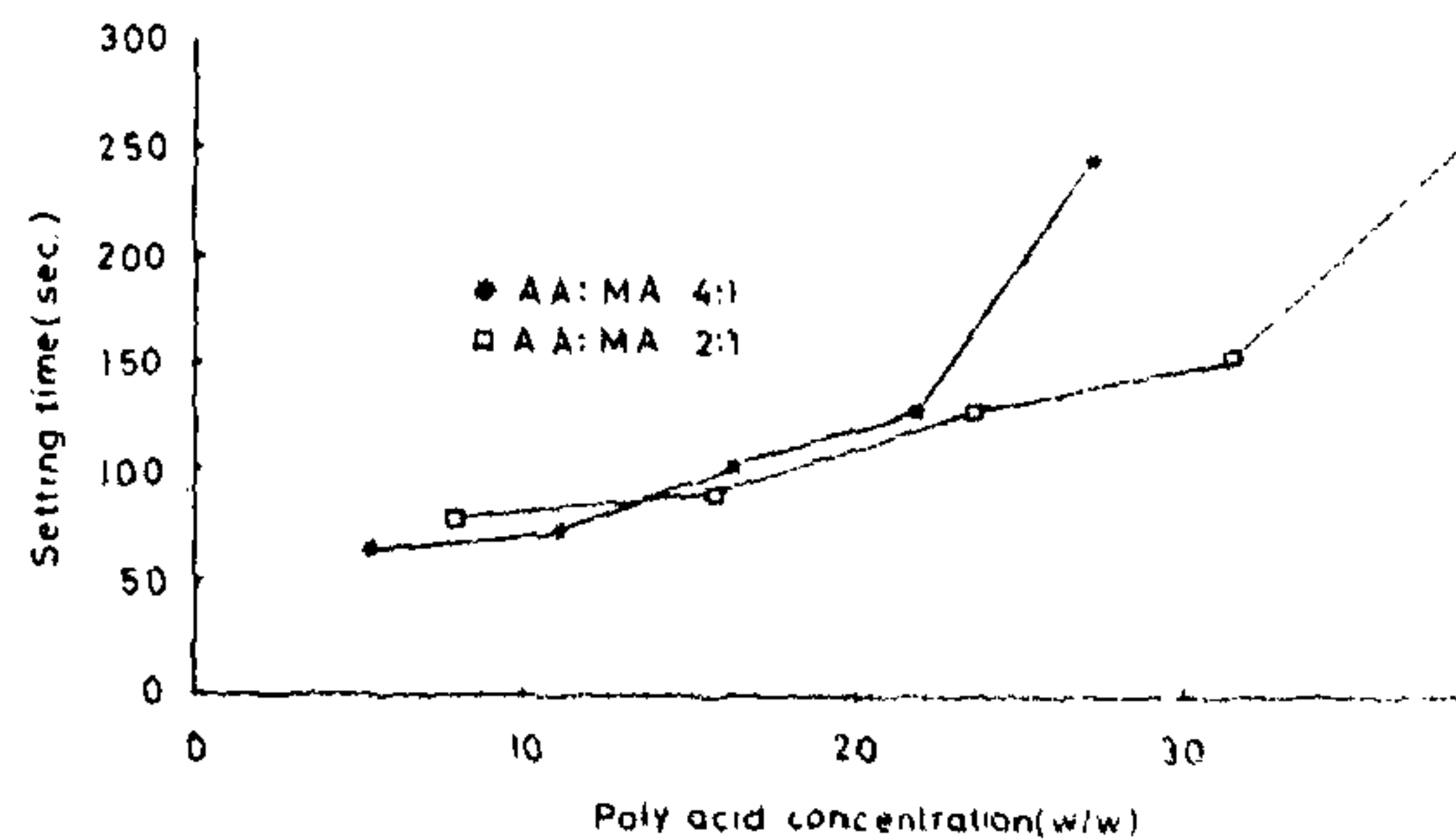


Figure 2. Effect of polyacid content on the setting time of poly(acrylic acid-co-maleic acid 4:1) [*] and poly(acrylic acid-co-maleic acid 2:1) [□] when reacted with glass.

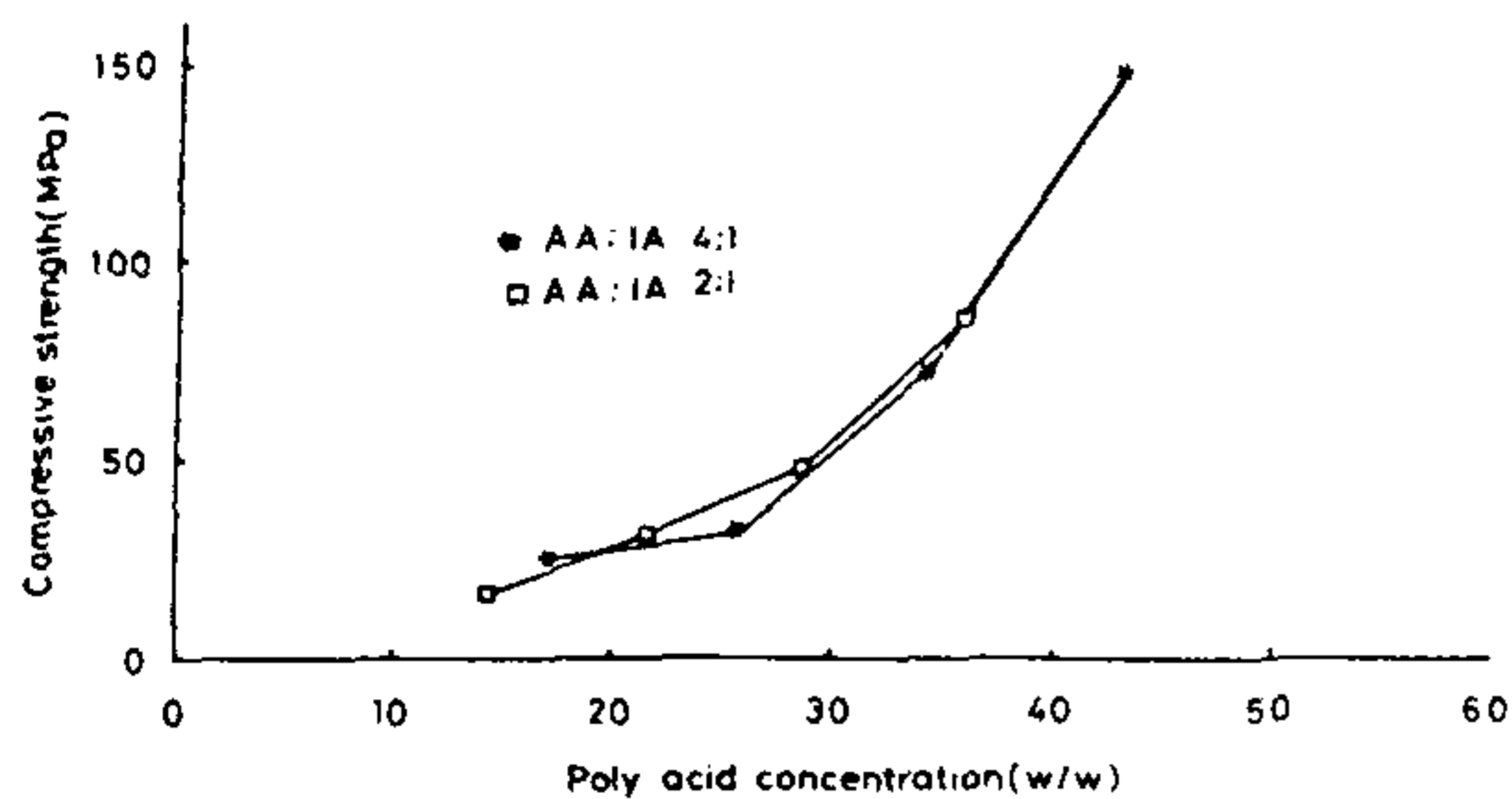


Figure 3. Effect of polyacid content on the compressive strength of cement formed when poly(acrylic acid-co-itaconic acid 4:1) [*] and poly(acrylic acid-co-itaconic acid 2:1) [□] is reacted with glass.

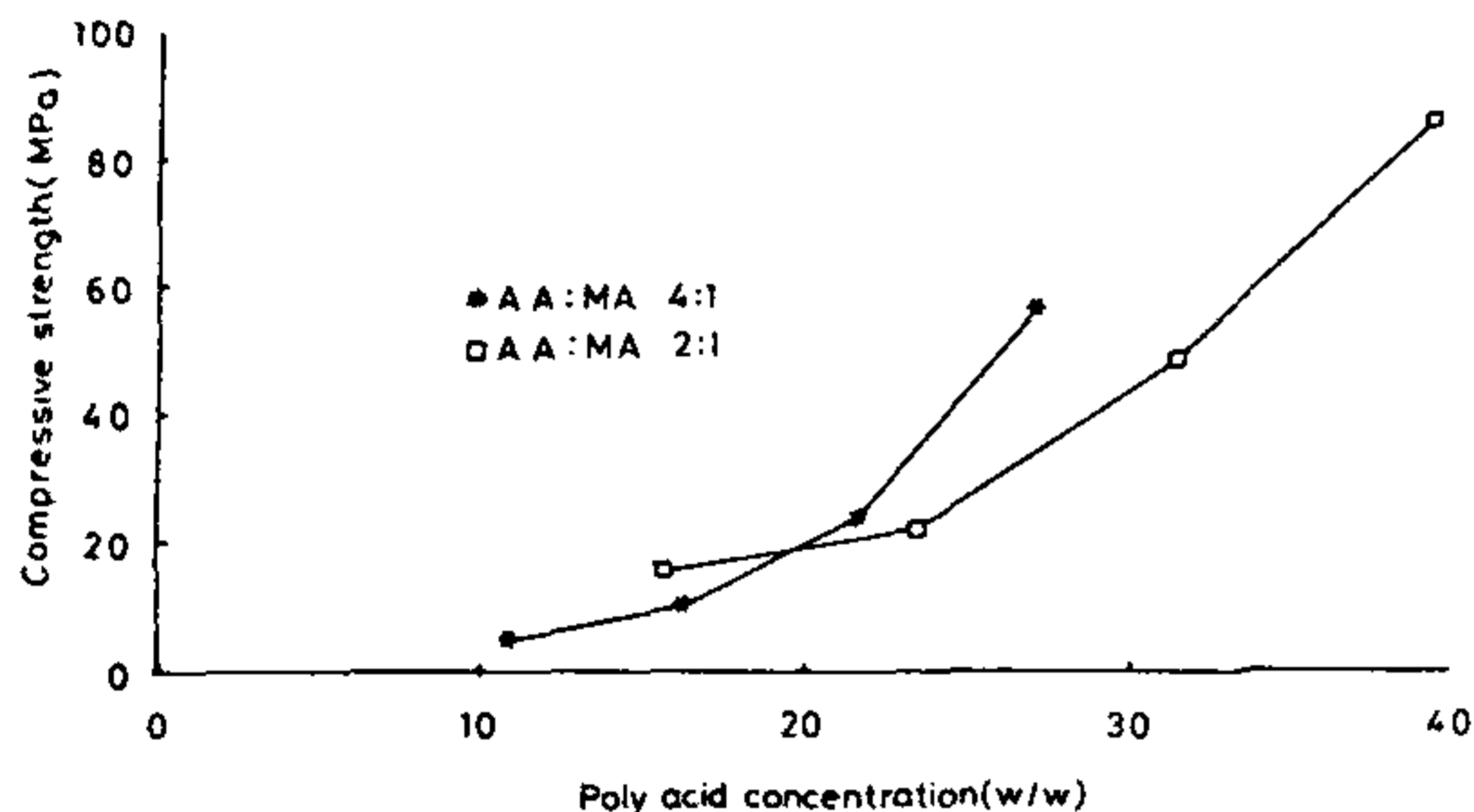


Figure 4. Effect of polyacid content on the compressive strength of cement formed when poly(acrylic acid-co-maleic acid 4:1) [*] and poly(acrylic acid-co-maleic acid 2:1) [□] is reacted with glass.

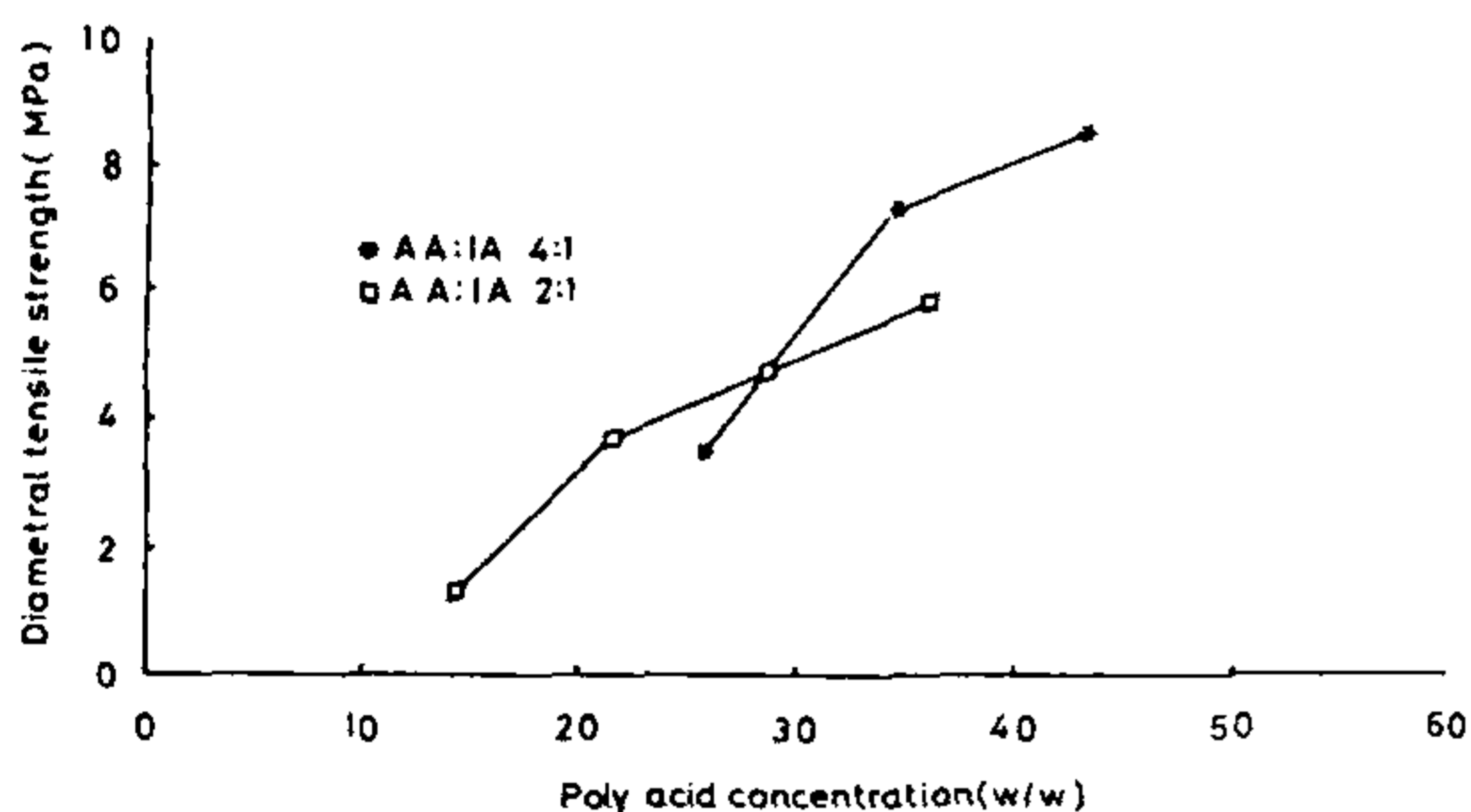


Figure 5. Effect of polyacid content on the diametral tensile strength of cement formed when poly(acrylic acid-co-itaconic acid 4:1) [*] and poly(acrylic acid-co-itaconic acid 2:1) [□] is reacted with glass.

change when polyacid content remained less than 25–30% by weight but above this value, they tended to show a sharp increase. Though setting time is mainly controlled by adjusting the ratio of alumina : silica in the glass fusion mixture and the fineness of the powder, Figures 1 and 2 show the prolonged setting times of the ionomer cements with increasing polyacid concentration for all four polyacids used. At low polyacid content levels, the setting took place within 100 s and working

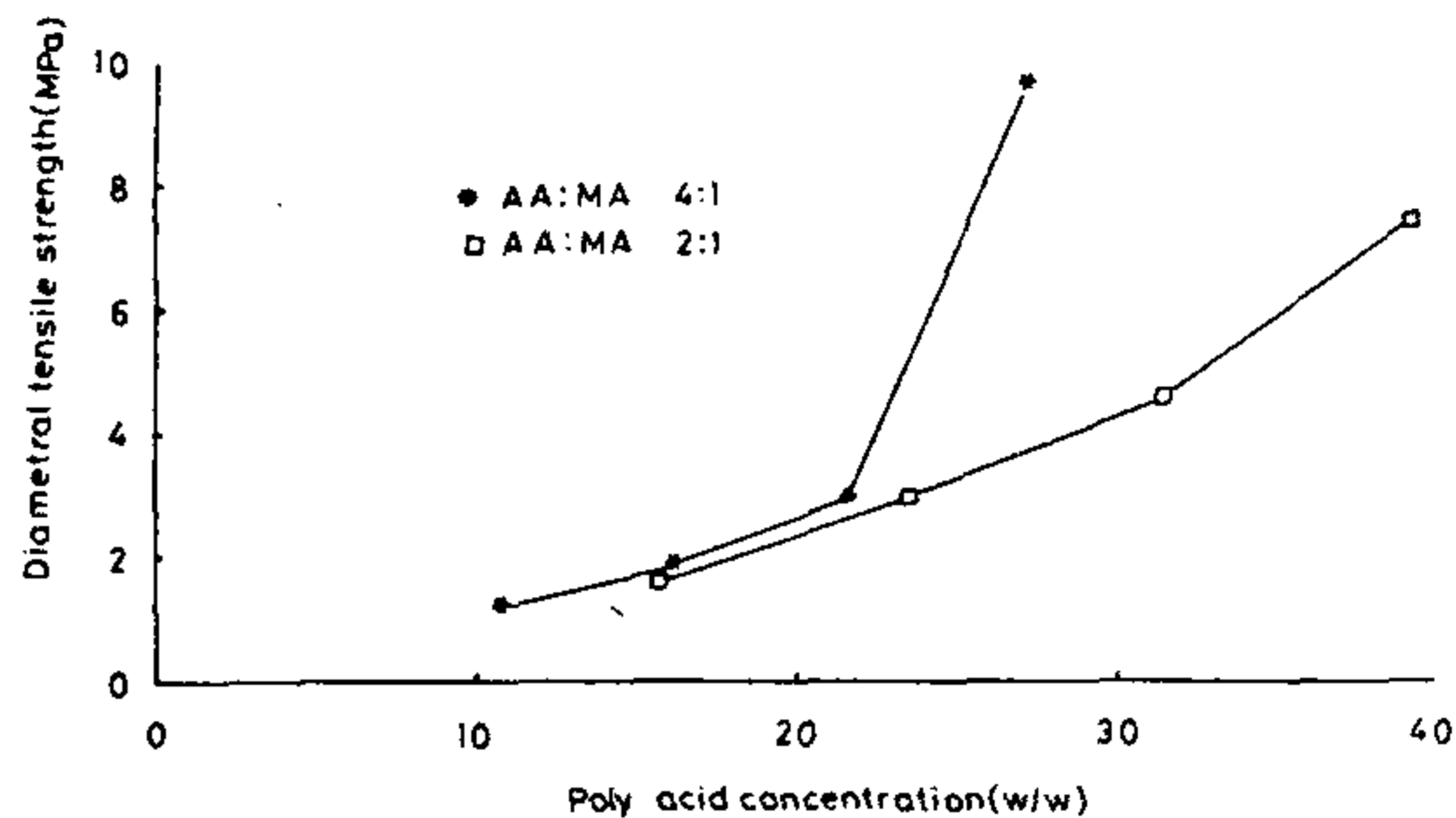


Figure 6. Effect of polyacid content on the diametral tensile strength of cement formed when poly(acrylic acid-co-maleic acid 4:1) [*] and poly(acrylic acid-co-maleic acid 2:1) [□] is reacted with glass.

times were found to be relatively low, which was highly disadvantageous from a practical point of view. However when polyacid content increased, handling of the cement became easier, which accounted for adequate setting time (3–5 min). A concentration of nearly 35–40% of polyacid was found to give optimum setting times. Both itaconic and maleic acid systems tended to show the same behaviour. In the set cement, the glass filler actually contributes to the formation of its own matrix within which the filler consists of an unreacted glass core sheathed by a layer of silica gel binding the glass particles together effectively into a cement.

The compressive and diametral tensile strength values of the glass ionomer cements showed a sharp increase with increasing polyacid content (Figures 3–6). Of all the four polyacid systems used, poly(acrylic acid-co-itaconic acid 4:1) having a polyacid content of 30–40%, when reacted with glass powder, showed the greatest compressive and diametral tensile strength. Poly(acrylic acid-co-maleic acid 4:1) system also showed good mechanical properties at the same polyacid content level. The compressive or tensile strength values do not extrapolate to zero at zero polyacid concentration, which indicates that when the acid content decreases below a certain value, the structure of the polyalkenoate cement changes. A critical concentration must exist at which the mean distance between the polymer molecules in aqueous solutions becomes too great for crosslinking to contribute significantly to the structure with consequent loss of strength. At high polyacid concentrations (>40%), the liquid is too viscous for practical use and is of theoretical interest only.

The increase in polyacid content above 30% by weight in the liquid part of the glass ionomer cement is found to prolong the setting reaction for all four polyacid systems studied. The mechanical properties are, however, improved considerably at higher polyacid content.

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Accumulated and fractionated anorthosites from the Ravipadu gabbro pluton, Prakasam province, Andhra Pradesh, India

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The Ravipadu gabbro pluton contains two types of anorthosites formed by accumulation and fractionation. The cumulate anorthosites (CA) are coarse grained and show characteristic cumulate textures whereas the fractionated anorthosites (FA) are medium grained and exhibit typical hypidiomorphic textures. The inferred crystallization sequence in CA is ol+pl, opx and cpx and in the FA is ol (+opx), cpx, pl, Fe-Ti oxides and apatite. The CA shows higher SiO₂, MgO, CaO, Al₂O₃, (Na₂O + K₂O) and Mg number and, lower TiO₂, Fe₂O₃, FeO, (Na₂O + K₂O) and P₂O₅ when compared to the FA. The normative $an/(an+ab)$ value is 0.74 in CA and that in the FA is 0.66. The CA contains lower Cr, V, Zn, Rb, Sr, Y, Zr, Nb, Ba, Ta, Pb, Th and U and, similar Sc, Co, Ni, Cu, Ga and Hf when compared to FA and this is in accordance with their modal mineralogy and process of formation. In the primary melt-normalized REE diagram the CA shows positive Eu anomaly in contrast to the fractionated one which shows negative Eu anomaly. It is suggested that accumulation of early-formed plagioclase crystals along with minor mafic minerals has resulted in the formation of the CA and fractionation of mafic minerals from the parental basic magma has delivered the FA. Field evidences suggest that the CA is formed by *crystal floatation*.

ANORTHOSITE is a significant member of the Archaean layered complexes, Proterozoic massifs, Bushveld type layered bodies and also small basic plutons¹. The anorthosites associated with the basic plutons are formed

either by accumulation of early-formed plagioclase crystals or after fractionation of mafic minerals, from a parental basic magma. The latter kind of anorthosites form a class by themselves and they occur without any temporal or spatial restrictions and characteristically display magmatic textures². The textural and geochemical features of anorthosites produced by both the processes are diverse and unambiguously reflect the mechanism of their formation.

In the Prakasam province^{3,4}, Andhra Pradesh, basic plutons with integral anorthosite/gabbroic anorthosite members occur at Boggulakonda, Settopalle, Purimetla, Pasupugallu, Chimakurti, Ravipadu and Kellampalle⁵. These are considered to be surface manifestations of subsurface high density material at a shallow depth. All these gabbro-anorthosite plutons have intruded along a major thrust fault between the Eastern Ghats Mobile Belt (towards east) and Dharwar craton (towards west) as delineated by gravity and DSS studies^{6,7}.

The Ravipadu gabbro pluton (RGP; 15°31'20"N; 79°48'15"E) is a post-tectonic lopolith which intruded into the Precambrian amphibolites^{8–10}. It is roughly elliptical in shape and occupies an area of 40 sq km. The RGP is composed of abundant olivine gabbros, subordinate olivine norites and troctolites and, minor but significant anorthosites. The present paper deals with the origin of two contrasting anorthosites from the RGP. These two varieties of anorthosites are termed cumulate anorthosites (CA) and fractionated anorthosites (FA).

In the field, anorthosites are better exposed than the gabbros due to the fact that they are relatively more resistant to weathering. The CA occur as a crescent shaped body within troctolites in the pluton. They are coarse grained (0.3 to 1.5 cm), heavy and characteristically dark grey to black in colour. These anorthosites can be distinguished from the surrounding troctolites by their freshness. Plagioclase is dark grey in hand specimen and commonly shows a considerable range in grain size.

The FA are sporadically present towards peripheries of the pluton within olivine gabbros. They are medium grained (0.2–0.4 cm), less heavy and light grey in colour and, glitter in the hand specimen due to the presence of clots of biotite. Glittering appearance distinguishes them from the surrounding olivine gabbros.

The CA and FA show textural diversity and variation in the mafic mineral content (Table 1). Under the microscope, the CA exhibit cumulate textures (Figure 1a). Plagioclase and olivine are the cumulus phases and, orthopyroxene, clinopyroxene and rarely opaque oxides form intercumulus phases. These anorthosites are adcumulates, and intercumulus pyroxenes are predominant over cumulus olivine. The plagioclase is euhedral to subhedral and contains oriented slender microlites of ilmenomagnetite (Figure 1b), which possibly imparts a dark grey colour to the rock¹¹. The plagioclase shows considerable adcumulus growth resulting in anhedral