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Fracture morphology and mechanical properties of thermocatalytically polymerized MMA-impregnated mortar

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Mortar mixes with different water–cement ratios and consistency were impregnated with methyl-methacrylate monomer and polymerized thermally under water using the free radical initiator α, α'-azobis (isobutyronitrile). Results on drying, impregnation and polymerization are presented. It is shown that a considerable amount of polymer remained strongly adhered or chemically inserted in the inorganic matrix. The molecular weight of the inserted polymer is higher than that obtained in the solvent extracted polymer and this is also higher than the polymer molecular weight obtained by bulk polymerization under the same conditions. The compressive and flexural strength of the impregnated mortar were found to be a function of the amount of polymer in the composites. Fracture behaviour under load, and polymer distribution inside the composites were examined by scanning electron microscopic techniques (SEM). It was observed that the polymer acts in two ways, first as a filler of porous and microcrack voids, secondly forming an anisotropic irregular network improving the bond characteristic of the interface between aggregate and matrix. Furthermore, due to the the adhesion of the polymer to both phases, it acts as a reinforcement and improves the mechanical properties, in particular the flexural strength.

1. Introduction

Soon after synthetic organic polymers appeared, they were reinforced and filled with traditional organic substances (wood shavings, plant fibres) or inorganic (minerals, fibreglass) in order to improve the physical properties and also the economic advantages. Recently different techniques are being employed to obtain new types of structural composites materials by impregnating wood, bricks and hardened mortar or concrete with monomers, being then polymerized *in situ* by radiation or thermocatalytic intitiation in order to fill the porous void volume with polymer [1, 2]. In wood–plastic combinations (WPC) and polymer impregnated concrete (PIC), the composite phases are changed so that the plastic is now the filling material. However, not all combinations give rise to true composites, in the sense that composite materials should have properties that are equal or superior to the sum of the properties of the constituent materials [3]. This depends on the original properties of the wood and concrete as matrices and the properties of the polymers as fillers. Low-cost common plastics have poor physical properties when compared with the strong cellulose fibrils but better tensile (σ_T) and compressive strengths (σ_C) than the concrete. As an example of this, the σ_T and σ_C for poly methylmethacrylate (PMMA) with a density of $\rho = 1.19$ g cm^{-3} are around 665 and 1.015 kg cm^{-2}, while the wood with $\rho = 1.14\,g\,cm^{-3}$ are 1.354 and $1.056\,kg\,cm^{-2}$ and for the concrete with $\rho = 2.4\,g\,cm^{-3}$ 20 and $250\,kg\,cm^{-2}$. Another important factor in obtaining composites with improved physical properties is the interaction or bonding between the matrix (wood or cement paste) and the organic polymer. Direct observation of fracture surfaces indicates little bonding between the polymer and cellulose fibres in WPC [3, 4], this being different from PIC, where a good interaction between matrix and polymer was found [5, 6]. Bearing in mind these observations, in WPC with 30% to 40% polymer by weight, relatively little improvement, or even deterioration of some properties (e.g. toughness) is observed, when compared on a per unit incremental density basis [4]. On the contrary for PIC, dramatically improved properties over those of conventional concrete were obtained with an addition of 5% to 7% of polymer [7]. Due to these results, we became more interested in the research of PIC considering that the cost of the polymer is the main factor in the development of these composites [8].

From the beginning, PIC systems have been obtained mostly by applying the radiation process for polymerization, carried out in air on wrapped samples to hinder monomer loss by evaporation and drainage [1, 9–12]. In this research the polymerization of the monomer was achieved by a thermocatalytic process under water in order to make the production process easier and less expensive. Methyl-methacrylate (MMA) monomer was employed for impregnation of the mortar [8, 13]. A great number of studies have dealt with the influence of some variables during the preparation of the sample (mixing, curing, drying, vacuum, evacuation time, soaking, monomer types, etc). and polymerization [9–12]. However, very little research has been done to analyse the polymer distribution inside the composite and the bond characteristics between aggregate and matrix due to presence of the polymer [5, 6].

2. Experimental

2.1. Mortar composition and sample preparation

In order to obtain specimens with different porosities, seven mortar mix series, each of 12 specimens, were prepared employing 0.35, 0.50 and 0,70 water–cement (*w/c*) ratios and also different consistencies by changing the sand content. Three different consistencies were used namely dry, normal and plastic (Table I). Furthermore, in the case of the 0.50 *w/c* specimens with a plastic consistency, three other series were cast. These series were impregnated with monomer containing different catalytic concentrations in order to change the polymer molecular weight.

The mortar samples were cast into a 4 × 4 × 16 cm beam moulds which were placed in a moist room (20° C, 95 r.h.) for 24 h until demoulding. They were then immersed in lime water for 28 days. Portland cement Type I was used in all experiments.

2.2. Drying, evacuation and impregnation of specimens

After curing, the specimens were oven-dried at 110° C. It appears that the drying temperature employed removes most of the free water without seriously affecting the strength of the PIC composite. The samples were then kept in a desiccator until impregnation by a procedure described elsewhere [4], i.e. previous evacuation of the specimens at a pressure of 10^{-2} mm Hg and held at this pressure for 4 h in order to improve the efficiency of monomer loading. The monomer-containing the catalyst was then introduced maintaining the vacuum during this time. The optimum impregnation time was 6 h [6]. The monomer loading in the mortar was determined by weighting the specimens before and after they were fully impregnated. This has been defined as the ratio of weight of monomer to the weight of dried impregnated material.

2.3. Polymerization and polymer characterization

The monomer used for impregnation of samples was commercial grade methyl-methacrylate (MMA) from Aldrich Chemical Co., due to its polymerization facility and good mechanical properties in the formed PIC composites. In most of the series, the monomer containing the inhibitors was mixed with 0.0278 mol of catalysts by litre of monomer (0.48% catalyst by weight of monomer). In order to produce polymers with different molecular weights, the series 4, 5 and 6 were impregnated by dissolving varying concentration of catalysts in the monomer, e.g. 0.115 and $0.011\,mol\,l^{-1}$ of monomer (1.89% and 0.01% catalyst by weight). Furthermore, small samples of monomer in penicillin ampoules were also prepared to study the bulk polymerization process at the same conditions.

The catalyst selected for this study was α, α′–azobis (isobutyronitrile) (AIBN) because it is easy to handle, sufficiently stable at room temperature, has a lower thermal decomposition than the benzoyl peroxide, and gives better mechanical properties for PIC [14].

Thermocatalytic polymerization in hot water was used in this research work because previous results suggest that it has no detrimental effects on the properties of the PIC composites and has potentially economic advantages when compared with other encapsulation method [15]. Mortar-impregnated specimens and bulk monomer samples were polymerized under water at 75 ± 0.1° C for 24 h until the reaction was completed. In an attempt to reduce monomer evaporation and drainage losses, the water was saturated with monomer and the specimen kept below water surface. Under these conditions practically no monomer depth is observed in the impregnated specimens. Unreacted monomer was removed by drying the specimens under vacuum. The amount of polymer formed was obtained by weighing the specimens before and after polymerization.

The PMMA formed inside the mortar specimens was extracted in a Soxhlet apparatus by using methylethyl ketone as a solvent.

The impregnated specimens were finely ground and the powder extracted by refluxing repeatedly at 81° C. The solution with dissolved polymer was then centrifuged at 6000 rpm for 30 min in order to separate the inorganic matrix. The extracted solution was added to methanol to precipitate PMMA, filtered, washed with methanol several times, and dried under vacuum at 60° C.

The PMMA remaining in the specimen could not be dissolved and was obtained by the digestion of the inorganic matrix with concentrated hydroflouric acid (HF). The polymer was purified by dissolving in methylethyl ketone, filtering through a fine glass filter, and finally precipitated in methanol. The molecular weight was determined indirectly by measuring the intrinsic viscosity with an Ubbelohde viscometer at 30° C in benzene and employing the following equation [16]:

$$(\eta) = 5.2 \times 10^{-2} \times \bar{M}_v^{0.76} \qquad (1)$$

2.4. Mechanical properties and fracture morphology

The mechanical properties of the composites were obtained by flexural tests of the prisms with centre point loading and compressive test of the broken parts. The fracture surface was analysed with a Cambridge scanning electron microscope model 600. The specimens, joined to the studs by a conducting adhesive paste, were observed under the microscope mainly without any metal covering to allow later the extraction of the polymer from the surface by dissolving with a solvent. In the other cases the specimens were placed in a vacuum evaporator and coated with a very thin layer of carbon followed by a gold layer of about 100 Å thickness.

3. Results and discussion

3.1. Impregnation and polymerization of specimens

Hardened cement-mortar consists of a dispersed fine sand aggregate held together by a continuous phase formed by cementitious hydrated paste. Due to the sand's scanty porosity, the bulk porosity of the material arises mainly from the cement paste or matrix phase. This porosity is made up of various different contributions. A small amount of fine gel porosity is formed by the reaction with water during the hydration cycle. The larger volume of porosity comes from the excess of water needed to make the mix workable and depends mainly on the original water-cement ratio and on the curing time. These capillary pores are responsible for the higher permeability of the composite [17]. If all the pores were filled with monomers it would be easy to calculate that the maximum weight loading in the composite would be about 6% to 7% [18]. However, because of the additional aggregate pores, air voids, and microcracks formed during the curing process, a larger amount can be obtained [19].

Although some works are concerned with impregnation of specimens without previous drying [5, 20] an excess of free or unreacted water occupying the total void space must be removed in order to reach a maximum monomer loading and to obtain satisfactory composite results [15]. Fig. 1 shows the wt % loss as a function of drying time for specimens with different consistency and the same water-cement ratio. The data indicates that at 110° C the average drying time required for 0.50 *w/c* ratio was 14 h. The length of time required to expell the free water for 0.35 *w/c* was the same, while for the 0.70 *w/c* ratio it was 26 h. The total percent of water loss for the same *w/c* ratios depends on the consistency of the mixes, that is, plastic > normal > dry. It can probably be attributed to the different shapes of the capillary net.

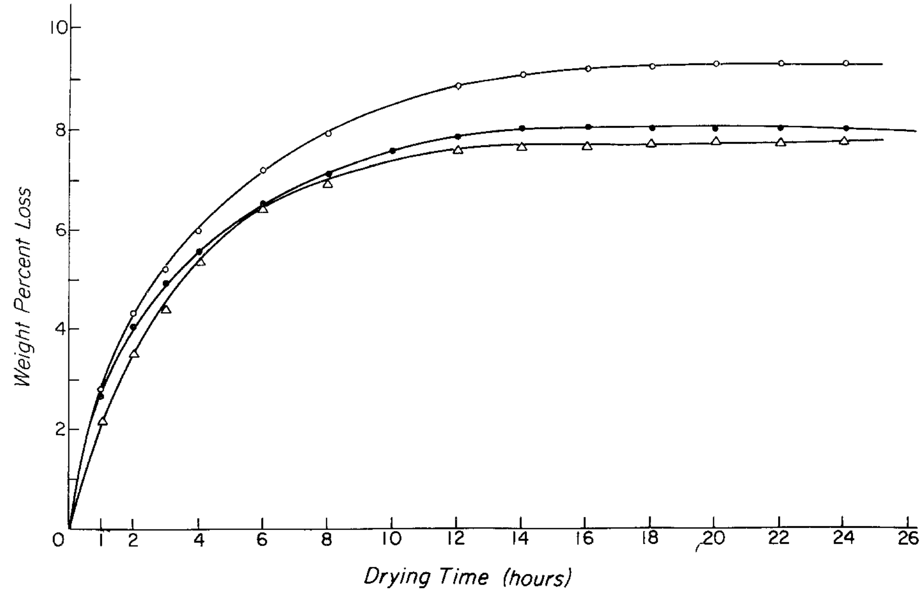

Figure 1 Drying curves for mortar specimens with different consistencies: ○ Plastic, ● Normal and △ Dry. Temperature 110° C.

The plastic specimens have in general a greater availability of continuous capillary pores, thus allowing the water to flow out easily.

The polymer loadings in the specimens previously soaked during 24 h in monomer, containing different amounts of catalyst, and without overpressure are shown in Table I. The polymer loading increases when *w/c* ratio is higher and for the same *w/c* ratio it also increases depending on the consistency in the same order: plastic > normal > dry. This is due to the variation of the total porosity, shape and dimensions of the capillary net occuring in the specimen because of the water excess.

The data of the conversion percentage of monomer to polymer inside the specimens are also given in Table I. The conversion is higher as the catalyst concentration increases (see series 4, 5 and 6). The reason is because dissolution of some monomer in warm water occurs during polymerization. By increasing the catalyst concentration, the polymerization rate is higher and the time to complete polymerization is shorter. The monomer loss using this method is about 10%, which is about the same amount as that previously reported [15]. On the other hand, due to the random nature of the polymerization mechanism, it is impossible to convert 100% monomer to polymer, and this gives rise to a thin layer free of polymer on the specimen's surface. The thickness of the layer depends on the catalyst concentration. Therefore, the specimens consist of a polymer impregnated inner core surrounded by a thin shell free of polymer (see Fig. 2). The thickness of the shell depends on the catalyst concentration and has a great influence in

TABLE I Mortar–polymer performed series; mix, impregnation and polymerization data

Series Number	Catalyst concentration (mol l^{-1} monomer)	Water/cement ratio	Sand/cement ratio	Consistency	Monomer loading (%)	Polymer loading (%)	Polymer yield (%)
1	0.0279	0.35	1	Plastic	8.34 ± 0.09	7.39 ± 0.08	87.67 ± 0.45
2	0.0279	0.35	2	Dry	6.80 ± 0.10	5.95 ± 0.11	87.50 ± 1.00
3	0.0279	0.50	2.5	Plastic	8.41 ± 0.18	7.14 ± 0.16	84.52 ± 0.54
4	0.1115	0.50	3.0	Normal	9.02 ± 0.09	8.19 ± 0.09	90.29 ± 1.04
5	0.0279	0.50	3.0	Normal	8.54 ± 0.08	6.94 ± 0.18	81.26 ± 1.25
6	0.0011	0.50	3.0	Normal	9.01 ± 0.08	6.49 ± 0.06	72.03 ± 0.49
7	0.0279	0.50	3.5	Dry	8.05 ± 0.11	6.73 ± 0.09	83.48 ± 1.34
8	0.0279	0.70	4.0	Plastic	9.87 ± 0.12	7.88 ± 0.14	79.83 ± 0.94
9	0.0279	0.70	5.0	Dry	9.19 ± 0.18	7.56 ± 0.08	82.21 ± 1.80

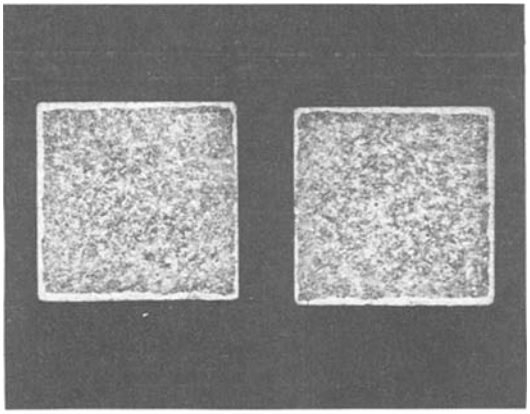

Figure 2 Cross-section of split polymer-impregnated mortar, showing the polymer-impregnated inner core surrounded by a thin shell free of polymer.

the mechanical properties, specially in the flexural strength, since in this case, the microcracks preceding the fracture, appear in the parts lacking of polymer.

3.2. Polymer extraction and characterization

The properties of the polymer formed inside the cement pores seem to be some of the less studied points [21]. The molecular weight would be the principal factor that determines the polymer's mechanical properties. The free polymer inside the specimens was obtained by extraction. The amount of extracted polymer (homopolymer) formed by different catalyst concentrations are shown in Table II, being in the range from 25% to 29%. Similar quantities were obtained by polymerization of MMA initiated by gamma radiation [6, 22] and by thermocatalytic initiation with benzoyl peroxide [23]. In the last case the molecular weight of PMMA as a function of polymerization temperature was determined as located through the cross-section of the specimen. It was found that at 70° C the polymer extracted varies between 15% and 40%, depending on the distance from the surface to the inner core of the specimen, giving rise to an average of 27.5%.

The rest of the polymer remained fixed by chemical or mechanical bonding in the inorganic matrix and could not be dissolved from the specimens by normal solvents (inserted polymer). In order to obtain the inserted polymer, the inorganic matrix was destroyed by treatment with concentrated HF. The molecular weight values of the homopolymer and inserted polymer are given in Table II and compared with those of the polymer prepared in bulk outside the mortar. The molecular weight of the polymer formed inside the specimen is unexpectedly higher than that obtained in bulk with the same catalyst concentration. Similar results have been found by the authors employing gamma radiation to initiate the polymerization [6]. These results do not agree with those proposed in the literature [9] where it is assumed that the inhibitor is destroyed due to the alkalinity or to the ingredients in the mortar mixture, which may explain the higher polymerization rate inside the specimens. If this occurs, a larger concentration of free radicals is obtained, and the molecular weight would therefore be lower. On the other hand, higher molecular weight than that formed in bulk, together with a higher polymerization rate, was also found by Beason and Mayhan [24, 25] in the radiation polymerization of MMA–kaolin clay composites. It was established in this case that the inorganic material had a catalytic effect on the polymer formation [6]. Furthermore, it is very interesting to note that the molecular weight of the inserted polymer is higher than the homopolymer. These results indicate that systematic

TABLE II Viscosity and molecular weight of PMMA formed in bulk and inside the mortar specimens

Series Number	Catalyst concentration (mol l^{-1} monomer)	Extracted polymer (%)	$[\eta]$	$\bar{M}_v$
Bulk	0.1115	–	0.222	62.000
4*	0.1115	28.6	0.393	132.000
Bulk	0.0279	–	0.510	186.000
5*	0.0279	25.0	0.631	236.000
Inserted polymer†	0.0279	–	0.701	272.000
Bulk	0.0011	–	0.829	353.000
6†	0.0011	26.4	0.838	358.000

*Homopolymer extracted by solvent of the series.

†Obtained by destroying the series 5 with HF after extracting the soluble polymer.

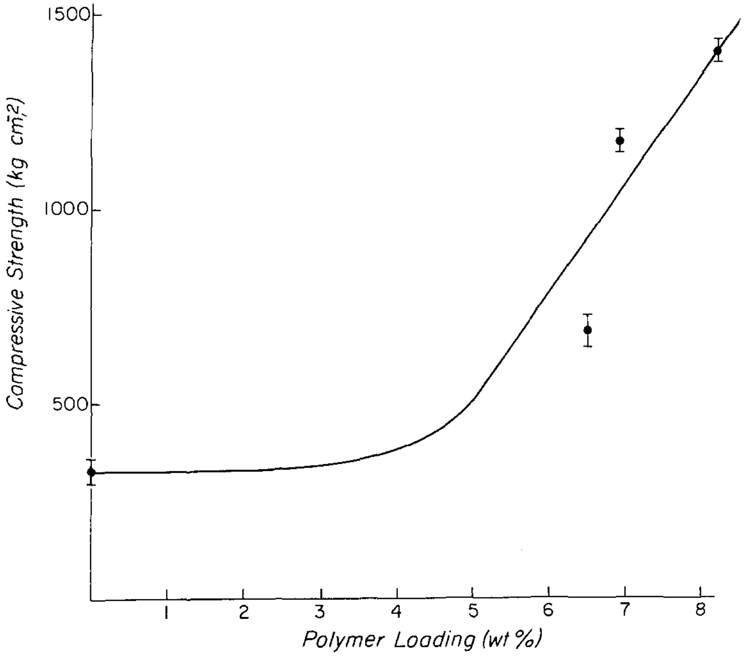

Figure 3 Compressive strength as a function of polymer loading.

research is necessary to determinate the mechanism through which the cement paste increases the polymerization rate and the molecular weight of the formed polymer. Finally, it appears that for the mortar mixes used the optimum catalyst concentration with respect to both polymerization time and polymer properties, would not be much higher than 0.115 mol l^{-1}.

3.3. Mechanical properties

In Fig. 3 the relationship between compressive strength and polymer content in the composite for series 4, 5, and 6 is shown. All of these correspond to mortar samples with a water/cement ratio of 0.5, plastic consistency, impregnated with the same monomer, but with different concentrations of catalyst. It was shown that the composite

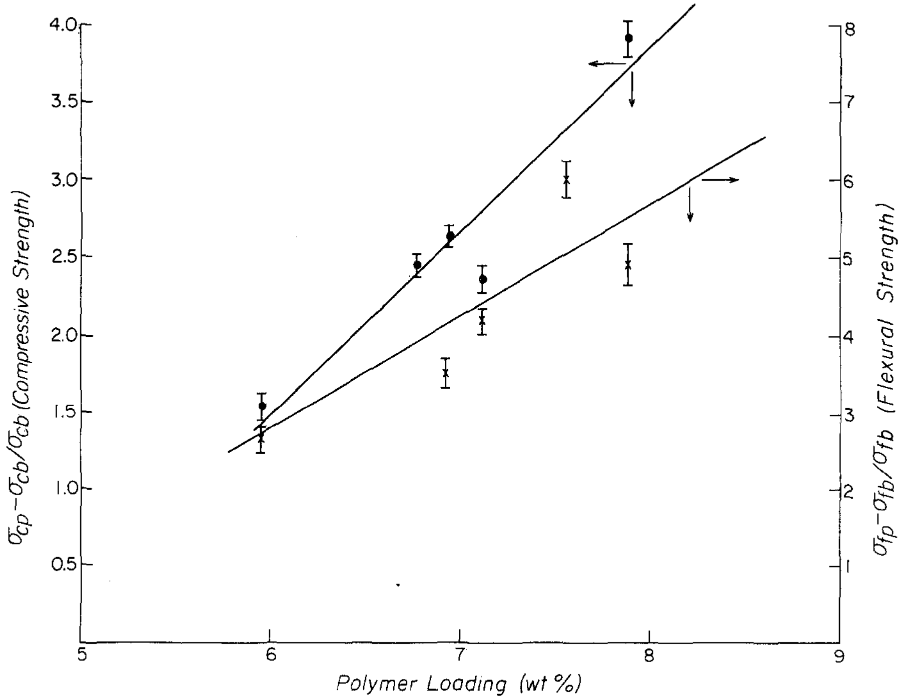

Figure 4 Incremental specific compressive and flexural strength as a function of polymer loading.

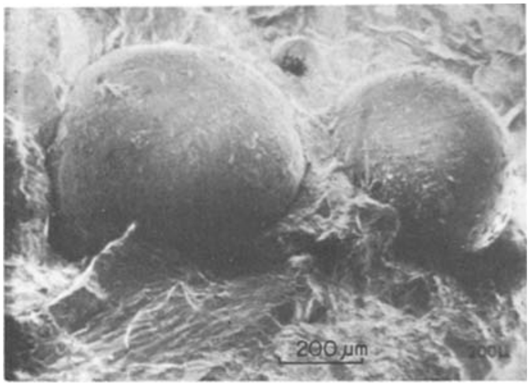

Figure 5 Fracture surface of PMMA–mortar composite shows sand bonded to the matrix.

strength is a function of the polymer content, and this content is also a function of the catalytic concentration. Furthermore, the initial porosity of the matrix does not appear to be the main parameter controlling the amount of polymer inside the composite.

The relationship between compressive strength, flexural strength and polymer content is shown in Fig. 4 in terms of the dimensional parameters

$$\frac{\sigma_{cp} - \sigma_{cb}}{\sigma_{cb}} \quad \text{and} \quad \frac{\sigma_{fp} - \sigma_{fb}}{\sigma_{fb}}$$

where σ_{cp} is the compressive strength of the composite, σ_{fp} the flexural strength and σ_{cb}, σ_{fb} the compressive and flexural strength of the sample without polymer. There exists a direct relationship between these dimensionless parameters which are a measure of the effectiveness of the impregnation and the polymer content expressed in percentage by weight of the composite. This effectiveness is greater on flexural strength than on compression, due to the fact that the polymer plays an important role as a filler of the microcracks that exists in the mortar before any load is applied, as was shown in the fracture observation.

The sensitivity of the material to these microcracks is greater when it is submitted to flexural loads, therefore the presence of the polymer improves the strength under these conditions more than in the case of compressive loads.

It appears from these observations that the reinforcing action of the polymer comes primarily from the filling of voids and pores of the matrix although this contribution was not quantified since in many cases those voids and pores were found half filled, and secondly, by filling the pre-existing microcracks. In the first case the increase in strength is due to the reduction of total porosity of the material. In the second, there is also a delay of the crack initiation and propagation and therefore an improvement in the mechanical properties.

3.4. Fracture surface observations

A careful study of a sufficient number of microphotographs revealed a large number of microcracks in untreated specimens. These microcracks can be due to the shrinkage of the cement paste during the curing period and the drying treatment, or formed while testing the mechanical strength. However the fracture surface of the mortar-impregnated specimens shows very few microcracks because these have been filled by the polymer, as shown schematically by Schorn [26]. Due to the good link between all the composite components less microcracks are formed in mechanical tests. In the case of mortar-impregnated specimens, a certain amount of sand bonded with the matrix by grafted polymer could be observed on the fracture surface (Fig. 5).

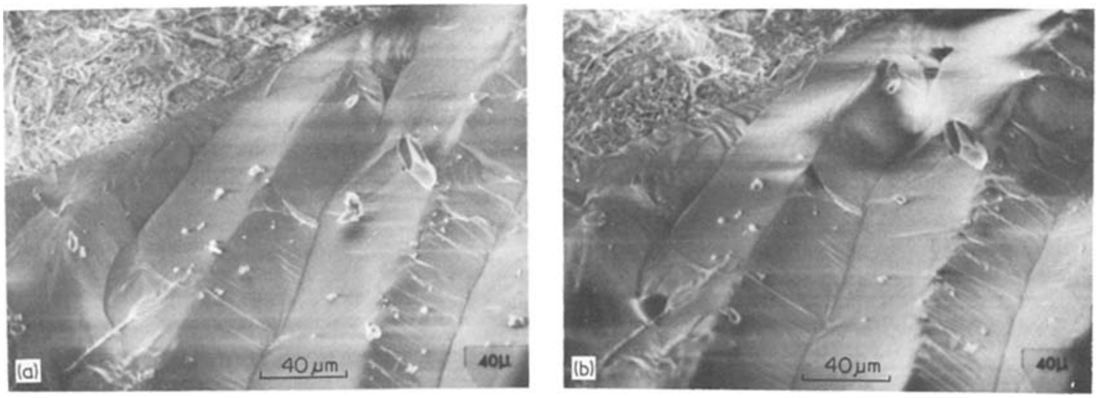

Figure 6 Fracture surface of PMMA-mortar composite (a) before and (b) after polymer extraction with solvent.

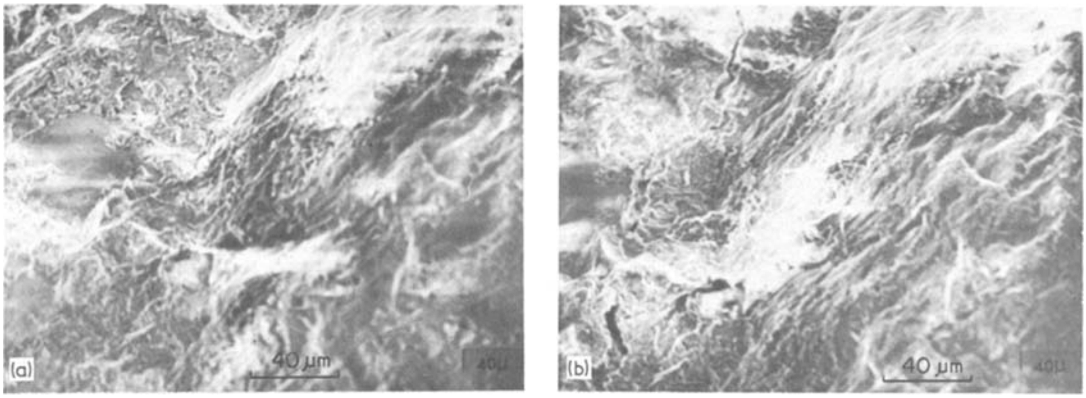

Figure 7 Fracture surface of PMMA–mortar composite (a) before and (b) after polymer extraction with solvent. Microcracks appear after polymer extraction.

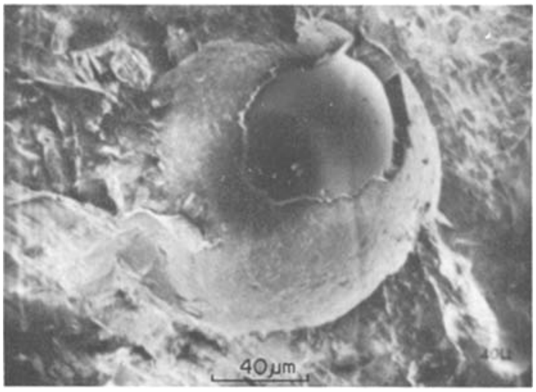

Figure 8 A macropore without polymer in fracture surface of PMMA–mortar composite.

A great deal of information on the polymer distribution in the composites was obtained by observing the same area of fracture surface before and after the polymer extraction by dissolution with solvent. The fractured surface of the polymer impregnated mortar, before and after polymer extraction, is shown in Figs. 6a and b. Both surfaces are relatively smooth and featureless, and no distinguishable polymer could be observed. This corresponds to the fine gel porous area consisting mainly of calcium silicate hydrate spherulites which had not been impregnated. On the other hand, it was found that the polymer appears to be filling the interface between the spherulites because of the larger spaces between them. Due to the polymer strengthening effect between the spherulites, the fracture occurs not only along the spherulite interface but also across it. This fracture mechanism is similar to the observed behaviour of a portland cement paste after two years of hydration [27].

By comparing the microphotographs of Figs. 7a and b, it can be seen that after polymer extraction previously unobserved microcracks appear. The fact that the microcracks existed before the mechanical test indicates that they had been filled by the polymer, repairing the deteriorated specimens and delaying the fracture. Furthermore, if these had been formed during the mechanical testing, the polymer inhibits the fracture initiation and propagation while strengthening the composite.

The relatively large number of macropores formed by entrapped air during mixing and casting, were found to be free of polymer because they were not connected to the capillary pore system (Fig. 8). The cracks were propagated through them. This pore formation should be avoided in order to obtain composites with better mechanical properties [8]. On the other hand some other macropores are connected to the capillary pore system, containing therefore a large amount of polymer as can be observed in Fig. 9a. By solvent extraction, the polymer is dissolved leaving its traces on the inorganic matrix (Fig. 9b).

From the above results it can be concluded that the polymer does not fill the specimens evenly and forms a discontinuous, anisotropic and irregular network inside the composite, depending on the shape and distribution of the capillary porous system.

Finally, a good bonding between the aggregates and the matrix is shown in the microphotographs

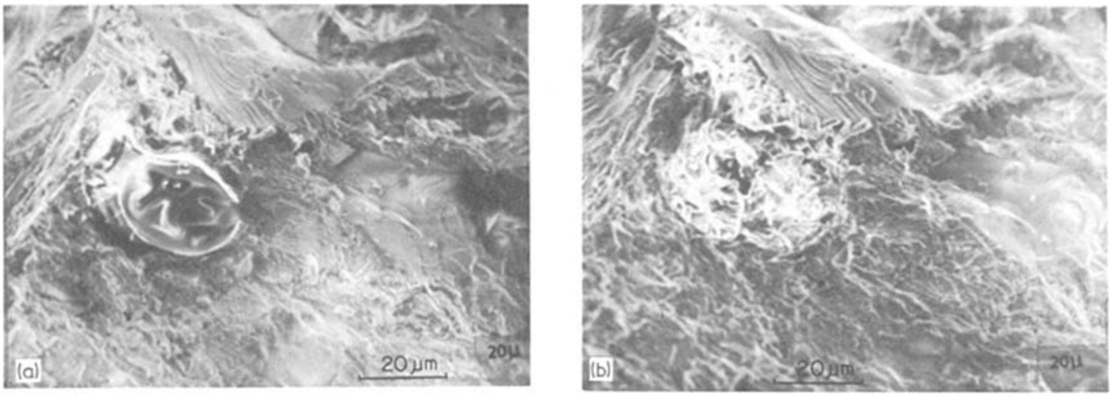

Figure 9 Fracture surface of PMMA–mortar composite; (a) before solvent treatment showing a large amount of polymer formed inside a macropore, (b) after solvent treatment the polymer is dissolved.

of Fig. 10. By treatment with solvent the polymer is dissolved and the aggregate is released, leaving its traces on the matrix surface.

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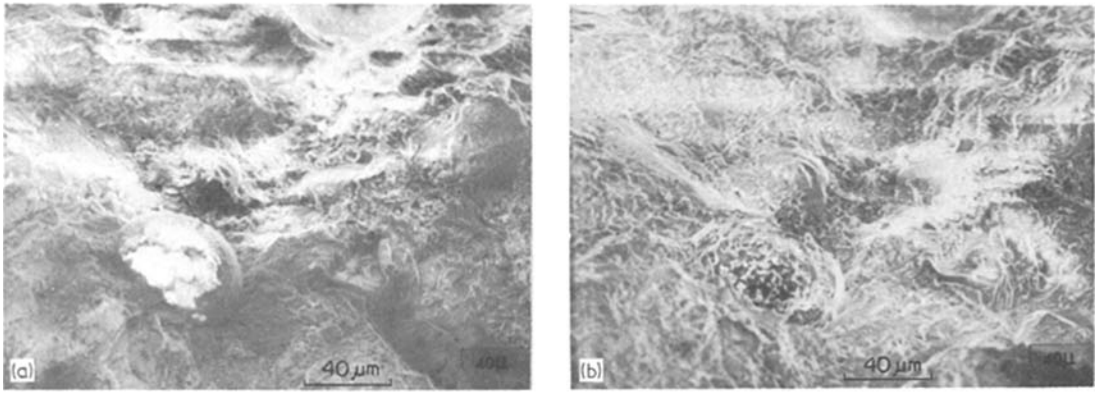

Figure 10 Fracture surface of PMMA–mortar composite; (a) sand bonded to the matrix by grafted polymer, (b) by treatment with solvent the sand is released leaving its trace on the matrix.

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