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S0958-9465(96)00001-7

Cement & Concrete Composites **18** (1996) 61–66

0958-9465/96/$15.00

Effect of Autoclaving on Cement Composites Containing Polypropylene, Glass and Carbon Fibres

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(Received 18 December 1995)

Abstract

The tensile properties of cement composites containing polypropylene networks alone and also hybrids of polypropylene and continuous glass or carbon fibres, were compared after curing at 20°C or 170°C in an autoclave. Although 170°C is nominally above the melting temperature of polypropylene, the fibres maintained a high proportion of their properties on cooling. Hybrids of carbon and polypropylene also survived autoclaving but the continuous glass fibres suffered severe damage in this curing regime.

Keywords: Autoclaving, fibre cement, carbon, glass, polypropylene, hybrids.

INTRODUCTION

All concrete materials need to be cured in a suitable environment to reach an adequate strength. Since an increase in the curing temperature of concrete increases its rate of development of strength, the gain of strength can be accelerated by curing in steam. High-pressure steam curing known as autoclaving was used for this research. Autoclaved concretes have several characteristics, as follows:

1. The ultimate strength can be obtained with short curing times (say within a day).
2. Efflorescence is less than general concretes because there is little water soluble $Ca(OH)_2$ in autoclaved concretes.
3. Shrinkage and creep are much smaller than general concretes cured in a humid condition.

In autoclaved concretes, different hydration products from those cured wet at atmospheric temperature and pressure are obtained. Thus, mix proportions have to be determined corresponding to the required properties of concretes. Autoclaving is curing with saturated steam at high temperature and pressure at over 100°C and generally carried out at a range of temperatures between 160°C and 200°C. Therefore, for fibre reinforced cements or concretes the abilities of the fibres to resist these high temperatures have to be considered.

The possible use of polypropylene as a fibre reinforcement for autoclaved cement products has generally been neglected because the melting point of the polymer is about 165°C and the softening point is about 150°C. Also, rapid oxidation could occur at these high temperatures if oxygen is present adjacent to the fibre. Tests in an oven in dry air at 170°C for 8 h showed complete embrittlement of the composite with extensive chain scission of the polymer. However, there is evidence[1] that the situation could be different in autoclaved products and hence this investigation was initiated. The work has practical significance because if polypropylene can be shown to survive autoclaving at around its melting temperature, the applications for polypropylene composites can be extended.

It has also been shown[2,3] that composites containing hybrids of different fibre types can have considerable advantages over single fibre composites and therefore hybrids of continuous

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Table 1. Mix proportions of matrix

Material	*Mix by weight*
Cement	1·00
Water	0·34
Silica sand	0·19
Pulverised fuel ash	0·25
Superplasticiser	0·016

polypropylene and glass fibres or polypropylene and continuous carbon fibres were also studied before and after autoclaving.

EXPERIMENTAL PROGRAMME

Matrix materials

The mix proportions of the matrix are shown in Table 1. This matrix had been used in the laboratory for many years for non-autoclaved products and therefore provided an excellent baseline of data with which the autoclaved products could be compared. It was not therefore optimised to be the best matrix for autoclaving because in this research the main interest was in the integrity of the fibres at high temperatures.

Hydrated silicates in the form of tobermorite are the most stable crystals in hydrated products which are produced with autoclaving. The more tobermorite which is produced, the smaller the shrinkage is and the stronger is the matrix which can be obtained. The product is varied by the molar ratio of CaO/SiO_2 and the best range of CaO/SiO_2 is 0·7–1·0.[4,5] In this report, curing in water was the standard and the ratio of CaO/SiO_2 was not considered for autoclaving. Assuming the contents of CaO and SiO_2 in a typical ordinary Portland cement are between 63 and 20%,[6] respectively, the ratio of CaO/SiO_2 is approximately 1·73 in this report. With this ratio, since the lime is in surplus, $\alpha 2CaO\ SiO_2H_2O$ is produced alone or coprecipitated with $Ca(OH)_2$ or tobermorite[4,5] and the strength of the matrix is expected to be reduced.

Fibres

The polypropylene fibres were 2-dimensional packs of continuous networks of stretched and split film supplied by Retiflex spa, Italy and were the same as used in commercial products. For these tests the lateral nets were removed from the pack so that all the fibres were approximately aligned with the direction of applied load.

The alkali-resistant glass fibre rovings were supplied by Cem-Fil International Ltd (Cem-Fil 2, Type 285/5). Each strand consisted of 100 filaments and the properties of the fibres are shown in Table 2. Typical data for glass fibre reinforced cement composites are given in Ref. 7.

The carbon fibres were continuous and consisted of strands with 2000 filaments of 10 microns diameter. They were type HM20-109 pitch-based carbon fibres supplied by Petoca Ltd, Japan. The properties are shown in Table 2. Some information on the properties of cement composites reinforced with continuous carbon fibres is given in Ref. 8.

Manufacture of composites and autoclaving

The composites were made by a hand layup technique with reinforcement patterns as shown in Table 3. The 64 strands in each glass fibre bundle were not bonded together but were spread out during specimen manufacture to ensure good contact with the cement paste. Each fibre layer was penetrated by cement paste before the next layer was added. Thickness of the sheets was generally between 5 and 6 mm, small thickness variations accounting for minor changes in fibre volume. The sheets were cut into strips 300 mm long and 25 mm wide after curing in water for 7 days and were sent to the Research Centre of the Asahi Glass Company Ltd. They were autoclaved with the temperature–time schedule as shown in Fig. 1.

Before increasing the temperature, the pressure in the vessel was reduced to −600 mmHg and maintained for 4 h. This treatment made the quantity of oxygen in the vessel low, which was thought to prevent the decomposition of the polypropylene by oxidation. Then the temperature was increased up to 170°C in 2 h and maintained for 9 h. After that, it was left to cool down below 100°C. The control specimens were cured in water at 20°C for about 60 days.

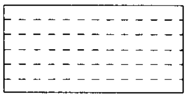
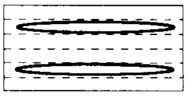
Tensile testing

Testing was carried out in uniaxial tension parallel to the fibre direction in an Instron 1122

Table 2. Properties of fibres

Property	*Glass Type 285/5*	*Carbon Type HM20-1091*	*Polypropylene networks*
Tensile strength (MPa)	1200–1700	2330	400
Elastic modulus (GPa)	72	210	15–5
Ultimate elongation (%)	2·4	1·11	8
Relative density	2·68	1·95	0·93
Filament diameter (microns)	14	10	Thickness 80
Filaments per strand	100	2000	—

Table 3.

Fibre volume fraction			Fabrication
PP(%)	GF(%)	CF(%)	
3.7	—	—	
4.6	—	—	
3.5	1.2	—	
3.7	—	0.6	

PP: Polypropylene networks - - - - - - - - - -
GF: Glass fibres (64 loose strands/bundle) ═══
CF: Carbon fibres ●

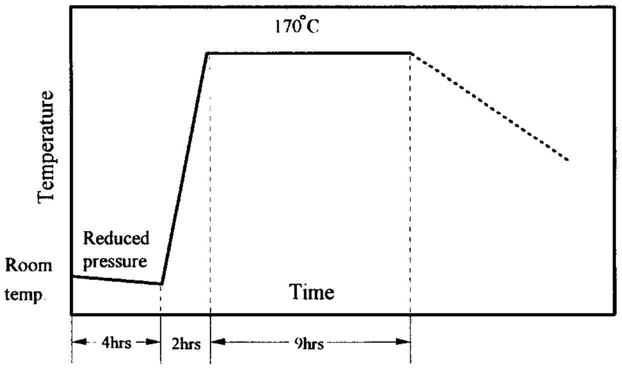


Fig. 1. Temperature–time schedule for autoclaving.

test machine. Strains on each side of the specimen were measured using linear variable differential transformers (LVDT) attached to a clip-on extensometer with 100 mm gauge length. The output was electrically averaged and a single load–strain plot obtained on an X–Y recorder. In order to determine accurately the uncracked composite elastic modulus and cracking strain, an X–Y–Y recorder was used simultaneously, where the strain output from the LVDT on each side of the specimen was recorded up to 0·5% strain at a larger magnification. The load signal was taken from the load cell. Also these signals were input into an Autonomous Data Acquisition Unit (ADU) system to enable automated calculation, analysis and graph plotting to different scales.

Details of the test system have been described elsewhere.[9] Crack spacings were determined after specimen failure.

RESULTS AND DISCUSSION

The general effects at 20°C of the addition of continuous glass or carbon fibres to the polypropylene reinforcement are shown in Fig. 2. The stiffer reinforcements give considerably improved post-cracking performance up to 1·5% strain but have reduced strain to failure. With respect to the polypropylene and glass fibre composite, after the glass fibres have failed, the polypropylene cannot sustain the applied load due to insufficient polypropylene fibre volume. On the other hand a small reduction after peak stress can be seen in the stress–strain curve for the polypropylene and carbon fibre composite. This reduction is thought to be caused by the local fracture of the carbon fibres. After the peak stress, the applied load has been transferred to the polypropylene

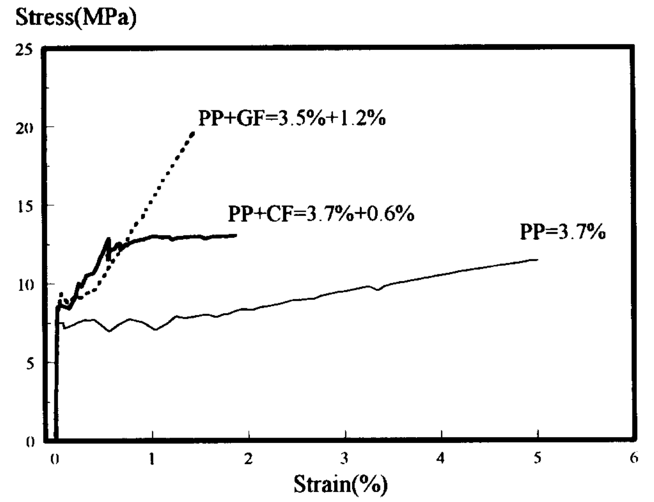


Fig. 2. Tensile stress–strain curves for composites cured in water. (PP: polypropylene, GF: glass fibre, CF: carbon fibre.)

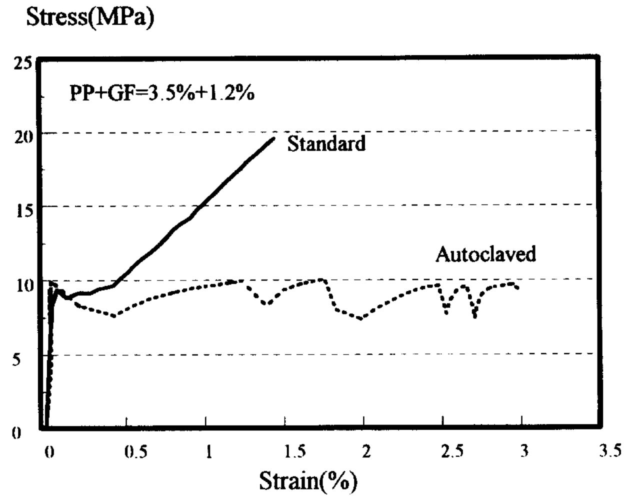


Fig. 4. Comparison between a standard and an autoclaved specimen reinforced with 3·5 vol% of polypropylene and 1·2 vol% of glass fibres.

networks to some extent, resulting in the ultimate strain of the polypropylene and carbon fibre composite (about 2%) being larger than the ultimate elongation of the carbon fibre (1·11%). However, the polypropylene fibre volume was not sufficient to allow the composite to be strained up to the 5% strain of the polypropylene-only composite. The reason that there is no descending curve in Fig. 2 is that all the fibres fracture at the maximum strain leaving no residual load capacity. The properties of hybrid composites are given in more detail elsewhere.[2,3]

Direct comparisons of stress–strain curves for water cured and autoclaved samples from the same sheets are shown in Figs 3, 4 and 5. Again, the end points of the curves are at fracture of the fibres so that there was no descending curve of the type often seen with short fibre pull out. Figure 3 shows the curves for samples containing 4·6% by volume of polypropylene networks only. It was rather surprising that in spite of the high curing temperature of 170°C, which is just over the melting point of unstretched polypropylene, the composite containing polypropylene still maintained its ductility on cooling even after 9 h at the elevated temperature. An explanation for this effect may be that although the polypropylene is at or above its melting temperature, the molecules in the stretched chains do not actually separate at this point but are effectively held in

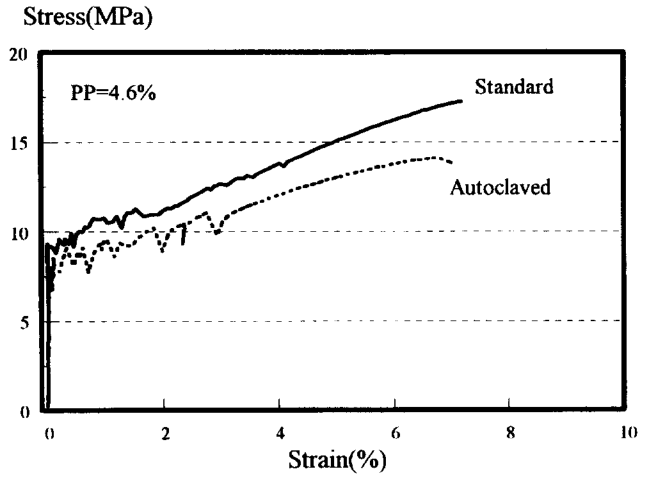


Fig. 3. Comparison between a standard and an autoclaved specimen reinforced with 4·6 vol% of polypropylene networks.

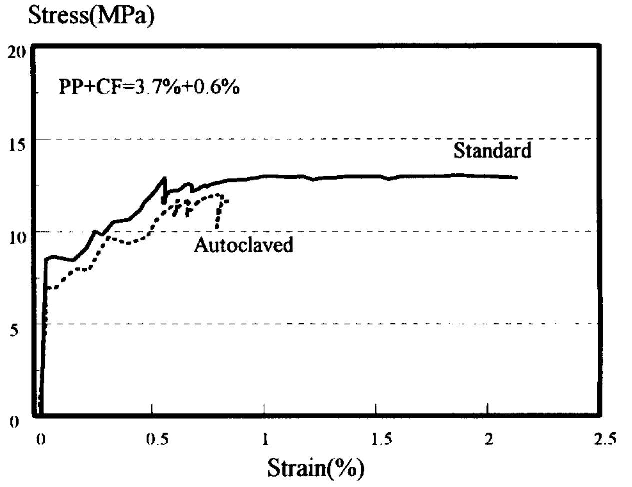


Fig. 5. Comparison between a standard and autoclaved specimen reinforced with 3·7 vol% of polypropylene and 0·6 vol% of carbon fibres.

their positions in the thin channels in the cement paste. On cooling therefore a high proportion of the unheated properties can be maintained or re-established. However, since the ultimate stress and strain of the autoclaved composite were lower than those of the standard composite, the polypropylene was thought to be damaged by the high temperature to a certain extent. The stress for the autoclaved composite at the bend over point was reduced and the stress was generally lower than that of the standard composite at a given strain. The strength of the autoclaved matrix was also lower than that of the standard composite probably because the ratio of CaO/SiO_2 was too high to produce tobermorite.

Figure 4 shows a comparison between a standard and an autoclaved specimen reinforced with polypropylene networks and glass fibres. In the stress–strain curve for the autoclaved composite, only the horizontal region could be seen after the bend over point and no enhancement of properties by the glass fibre was obtained. The horizontal part of the curve showed that the combined strengths of glass and polypropylene fibres had reduced to about the critical fibre volume. As it was known from Fig. 3 that the polypropylene had only reduced in stength by about 17%, considerable weakening of the glass fibres must have occurred. Although the softening point of the glass is 500–700°C,[10] the glass fibres were thought to be seriously damaged by the heat and alkali attack during autoclaving. The residual strain capacity was provided by the polypropylene networks.

Figure 5 shows the comparison between autoclaved and water cured samples containing a hybrid of carbon and polypropylene fibres. The autoclaved composite failed at less than 1% strain, because the volume fraction of the polypropylene was not enough to carry the additional load after carbon fibre failure and the polypropylene was slightly weakened by the heat during autoclaving. Apart from the damage to the polypropylene and the matrix, the carbon fibre seems to still play a role as a reinforcement. Therefore, the carbon fibre can be used in the autoclaved composite.

Due to the scales on the figures it is not possible for the reader to deduce all of the important parameters of the hybrid fibre composites. Representative tensile properties are therefore shown in Table 4. The strain to first crack in the composite (e_{mu}) was only slightly altered by autoclaving whilst the strength of the matrix (s_{mu}) was reduced by about 20%

Table 4. Representative tensile properties of standard and autoclaved composites

Sample no.		V_{fp} (%)	V_{fg} (%)	V_{fc} (%)	e_{mu} ($*10^{-6}$)	S_{mu} (MPa)	S_{cc} (MPa)	E_c (GPa)	e_u (%)	S_u (MPa)	S_{fpu} (MPa)	C.S. (mm)
ST	PP-1	4·69	—	—	260	9·37	9·10	35·0	7·88	16·97	362	4·2
	PP-2	4·65	—	—	280	9·28	9·03	32·2	7·19	17·21	370	3·6
	PP-3	3·73	—	—	270	7·58	7·44	27·5	5·00	11·42	306	4·2
	PG-1	3·74	1·23	—	320	9·12	9·12	28·5	1·44	19·54	—	1·8
	PC-1	3·43	—	0·55	280	8·54	8·66	30·9	1·87	13·01	—	3·9
AC	PP-11	4·38	—	—	310	8·51	8·33	26·9	5·69	14·46	330	8·3
	PP-12	4·59	—	—	310	7·47	7·33	23·7	6·72	14·06	306	12·5
	PP-13	3·68	—	—	300	7·43	7·31	24·4	4·65	10·67	290	12·5
	PG-11	3·34	1·14	—	300	7·10	7·17	23·9	2·44	9·17	—	25·0
	PG-12	3·45	1·15	—	350	7·72	7·82	22·3	2·95	9·67	—	16·7
	PC-11	3·83	—	0·64	270	7·06	7·25	26·8	0·97	11·99	—	12·5
	PC-12	3·70	—	0·61	310	7·37	7·61	24·6	0·84	11·62	—	16·7

ST: standard curing
AC: autoclaving
S_{mu}: strength of the matrix
V_{fp}: volume fraction of polypropylene networks
E_c: elastic modulus of the composite before the bend over point
V_{fg}: volume fraction of glass fibres
e_u: ultimate strain of the composite
V_{fc}: volume fraction of carbon fibres
S_u: ultimate stress of the composite
e_{mu}: first crack strain of the composite
S_{fpu}: ultimate stress of polypropylene ($=S_u/V_{fp}$)
S_{cc}: first crack stress of the composite
CS: crack spacing.

although still being of satisfactory strength at about 7·5 MPa.

The reduction of the elastic modulus of the composite E_c was caused by both the reduced modulus of the matrix and the fibres due to autoclaving. As a result of autoclaving, the strength and stiffness of the polypropylene networks were reduced, which resulted in the reduction of the ultimate stress and strain.

The strength of the polypropylene (S_{fpu}) in Table 4 was reduced from about 345 to 309 MPa showing some changes in the molecular structure.

The crack spacing in the case of the glass fibre composites PG-1, PG-11 and PG-12 had increased from about 2 to 18 mm which results from the complete loss of properties of the glass fibres resulting in the combined fibre volume not exceeding the critical fibre volume. However, for the rest of the composites the crack spacing had increased by a factor of about 3 times. According to Ref. 11, the crack spacing for fibre cements at more than the critical fibre volume is proportional to S_{mu}/τ where S_{mu} is the strength of the matrix and τ is the fibre–matrix bond strength. The strength of the matrix (S_{mu}) is known from Table 4 and therefore it can be deduced that there is a considerable weakening in bond between the polypropylene and the matrix due to autoclaving.

CONCLUSIONS

The polypropylene networks, which were the main reinforcement in the composite, were partly damaged by 9 h at 170°C in the autoclave but maintained sufficient properties to enable the use of polypropylene to be considered as a reinforcement in autoclaved products up to 170°C even though this temperature is above the melting point of the polymer.

The glass fibres used in this study were destroyed in autoclaving conditions but carbon fibres showed considerable promise as a reinforcement under high temperature steam curing conditions.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the assistance of the Asahi Glass Company in providing autoclaving facilities. Also, thanks are due to Dr R. Baggott of Salford University for suggesting the possible use of autoclaving for polypropylene composites. The help provided in supplying the fibres by Retiflex spa (Italy), Petoca Ltd (Japan) and Cem-Fil Ltd (UK) is gratefully acknowledged.

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