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Characterization of fibres from acrylic polymers for cement composites: DSC study[1]

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Abstract

The increasingly extensive use of synthetic organic fibres as reinforcement in cement composites requires a more detailed characterization of the fibres in order to estimate any interaction resulting from their addition to cementitious matrices. Research has thus been carried out on acrylic fibres derived from a homopolymer (PAN), and copolymers (AN–MA, AN–MA–IA), and on fibres derived from acrylic fibres (Oxid. PAN), by means of DSC and FT–IR, and SEM. Differential scanning calorimetry studies have been carried out, in both air and N_2 flow at different heating rates, by considering the typical exothermic effect and by estimating comparatively both the characteristic temperatures and the relative heats of reaction. These data, integrated and compared with FT–IR and SEM studies, can give useful information about the chemical and physical characteristics of the fibres.

INTRODUCTION

The introduction of synthetic fibres into cement composites often improves some of their properties [1,2].

In recent years, acrylic fibres or other fibres derived from them have been used more and more [1,3] because of their intrinsic properties (good tensile and breaking strain strength a non-critical diameter that avoids possible injuries to the respiratory tract, good thermal resistance, good resistance to acids and bases) and because of their availability on the market at reasonable prices.

Our study falls within this field: it concerns the total characterization of acrylic fibres from a homopolymer (PAN) and from copolymers (the weight percentage of monomer AN being greater than 90%), and of other fibres from a precursor of an acrylic fibre subjected to thermal treatment in an

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oxidizing atmosphere, producing such special properties as to make them good substitutes for asbestos fibres, as well as precursors suitable for the production of carbon fibres [3, 4].

Proceeding from the researches of the authors concerning different aspects of the use of synthetic fibres in mortar and concrete, the characterization of these fibres is necessary in order to identify possible alterations (hydrolysis of the functional groups, its extent, etc.) to which they have been subjected because of fibre–matrix interactions in hydrated and hardened cement composites.

For these studies, differential scanning calorimetry (DSC), together with FT–IR spectroscopy, are considered effective techniques. Scanning electron microscopy, showing the morphology of the fibres under study, has also been carried out.

EXPERIMENTAL

The acrylic fibres investigated are: fibres from a homopolymer (PAN), marketed as "Ricem"; fibres from an acrylonitrile and methyl acrylate copolymer (AN–MA) with monomers amounts of 93% and 7%, supplied by Enichem Fibre; fibres from acrylonitrile, methyl acrylate, itaconic acid copolymer (AN–MA–IA) of respective composition 93%–6%–1%, marked as "Sekril"; pre-oxidized fibres (Oxid. PAN) supplied by Enichem Fibre, obtained by thermal treatment of the acrylic fibres at about 250°C in an oxidizing atmosphere for about 3 h. This treatment makes the fibre infusible and non-flammable in air, reduces the value of the tensile strength by about 60% of the precursor fibre, and the fibre obtained is black.

The characteristics of the fibres are reported in Table 1.

The fibres submitted to DSC and FT–IR studies were cut in lengths of 1 mm. The DSC investigation was carried out using Du Pont 9900 equipment. The characteristic temperatures of the principal exothermic process (thermal degradation), the temperature range during which the reaction completes and the amount of heat evolved were estimated by

TABLE 1

Characteristics of the fibres

	PAN	AN–MA	AN–MA–IA	Oxid. PAN
Fibre length in mm	6	6	6	6
Diameter in microns	12.5	14.0	12.0	10.7
Modulus of elasticity in N mm^{-2}	23000	8260	15275	5287
Maximum enlargement %	9–10	16–17	19–20	15–20
Toughness in N mm^{-2}	805	600	–	350
Density in g cm^{-3}	1.18	1.18	1.18	1.38

TABLE 2

DSC data recorded for the fibres (heating rate, 20°C min^{-1})

	T_o/°C		T_p/°C		ΔH/J g^{-1}	
	N_2	Air	N_2	Air	N_2	Air
PAN fibre	305.0	315.0	312.5	326.0	237.9	1196.0
AN–MA fibre	311.0	306.0	318.0	314.5	318.2	662.0
AN–MA–IA fibre	284.5	262.5	300.5	285.0	315.9	796.4
Oxid. PAN fibre	267.0	284.5	361.5	342.0	136.0	262.5

TABLE 3

DSC data recorded for the fibres (heating rate, 10°C min^{-1})

	T_o/°C		T_p/°C		ΔH/J g^{-1}	
	N_2	Air	N_2	Air	N_2	Air
PAN fibre	288.5	297.5	296.5	308.5	340.7	1487.2
AN–MA fibre	292.0	285.0	300.5	302.5	366.3	824.2
AN–MA–IA fibre	269.5	252.0	289.0	268.5	350.5	888.4
Oxid. PAN fibre	249.0	266.5	336.5	331.5	116.0	262.9

calorimetric scannings in both air and nitrogen flow (50 ml min^{-1}). The values of T_o, extrapolated peak onset temperature, T_p, maximum peak temperature, and ΔH, heat of reaction, relating to the exothermic process are listed in Tables 2 and 3.

The FT–IR absorption spectra were recorded on a Perkin-Elmer model 1600 spectrometer (resolution, 4 cm^{-1}; scans, 16; duration, 1.0 min; range, 4000.0–400.0 cm^{-1}) on the fibres in the solid state, suitably prepared in the form of KBr discs. The micrographs were made on SEM-Philips PSEM 500 equipment.

RESULTS AND DISCUSSION

The scanning electron micrographs in Figs. 1 and 2 show, respectively, a fairly smooth surface with one lengthwise notch for PAN fibres, and a surface with light lengthwise striations for fibres from AN–MA copolymer. The surface of fibres from AN–MA–IA copolymer also have the same striations, but they are less marked.

Calorimetric scans, carried out at a 20°C min^{-1} heating rate, show for the PAN fibre an exothermic reaction with a clear peak at 312°C in nitrogen flow (Fig. 3(a)), whereas in air flow this effect appears at higher

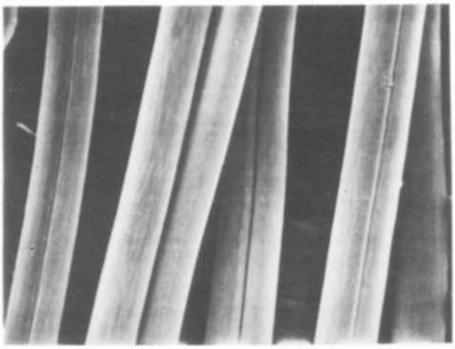

Fig. 1. SEM micrograph of PAN fibres: original magnification 400×.

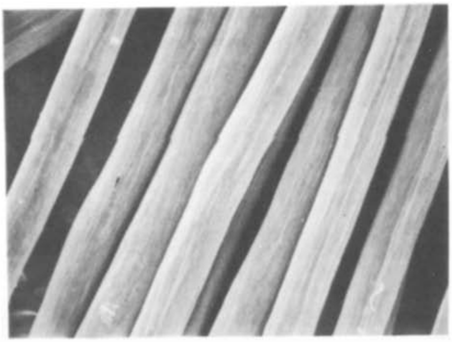

Fig. 2. SEM micrograph of AN–MA fibres: original magnification 400×.

temperatures and is developed over a large temperature range (Fig. 7(a)). In air flow the heat of reaction for this fibre ($\Delta H = 1196.0\ \mathrm{J\ g^{-1}}$) reaches a value higher than that in N_2 ($\Delta H = 237.9\ \mathrm{J\ g^{-1}}$) (see Table 2).

For the fibres derived from the copolymer, the T_p value of the exothermic reaction is lower in air flow than in N_2 flow (Table 2). For AN–MA–IA fibre, the decrease in T_p is more marked; in air or N_2 flow, both T_o and T_p are lower than those of the fibre derived from the homopolymer. For AN–MA fibre, in air flow the range of temperatures of the exothermic effect is

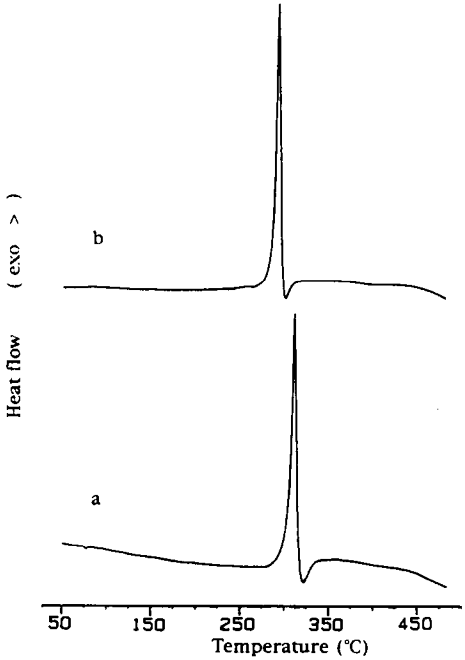

Fig. 3. DSC curves of PAN fibres in N_2 flow. Heating rate: (a) 20°C $\mathrm{min^{-1}}$; (b) 10°C $\mathrm{min^{-1}}$.

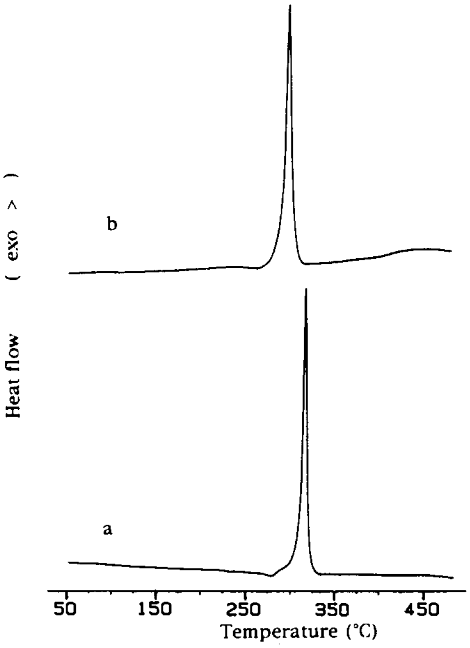

Fig. 4. DSC curves of AN–MA fibres in N_2 flow. Heating rate: (a) 20°C min^{-1}; (b) 10°C min^{-1}.

double that in N_2 flow (see Figs. 4(a) and 8(a)). The heat of reaction, almost equal for both fibres in N_2 flow, has different values in air flow: for AN–MA fibres it is 662.0 J g^{-1}; for AN–MA–IA fibres, 796.4 J g^{-1}.

It is assumed that in AN–MA–IA fibres the presence of the IA comonomer has a strong initiating effect on the exothermic reaction (see Figs. 5(a) and 9(a)). This hypothesis is in agreement with the observations of other authors [5, 6], relating to the thermal decomposition of powdered polymers and copolymers. The exothermic effect is the result of an endothermic contribution due to scissions and fragmentations in the molecular chains, and to an exothermic contribution that is mainly the product of the cyclization reactions of the nitrile group (CN) [5, 7]. In air flow, the cyclization reaction is influenced by the presence of oxygen. In fact the greater heat liberated under air can be attributed to the oxidization of some groups of the cyclized structure (thermal-oxidative degradation). If the characteristic temperatures of the exothermic effect are lower, as in the case of fibre from AN–MA–IA copolymer, the endothermic contribution due to the scissions and fragmentations decreases and, consequently, the total amount of ΔH increases.

The DSC results for the Oxid. PAN fibre show an exothermic effect that is lower than those of the acrylic fibres (Table 2), with a higher T_p and a larger temperature range (see Figs. 6(a) and 10(a)). The lower heat of

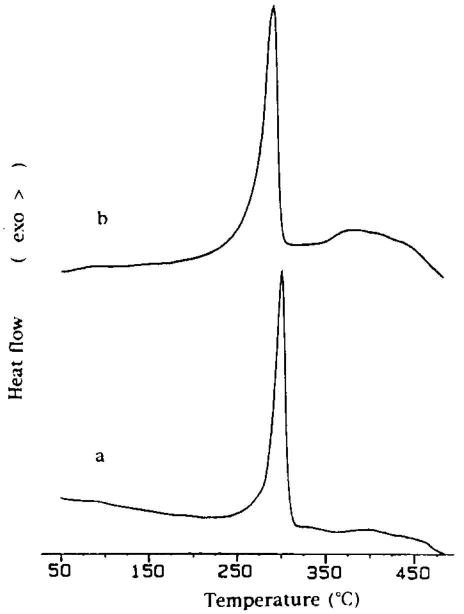

Fig. 5. DSC curves of AN–MA–IA fibres in N_2 flow. Heating rate: (a) 20°C min^{-1}; (b) 10°C min^{-1}.

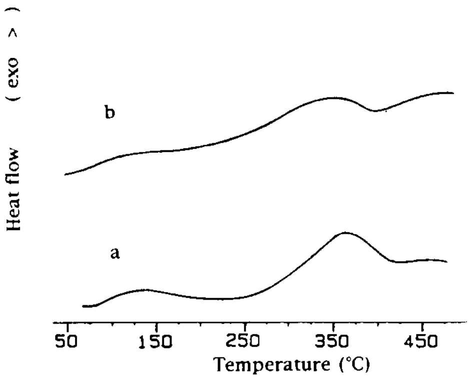

Fig. 6. DSC curves of Oxid. PAN fibres in N_2 flow. Heating rate: (a) 20°C min^{-1}; (b) 10°C min^{-1}.

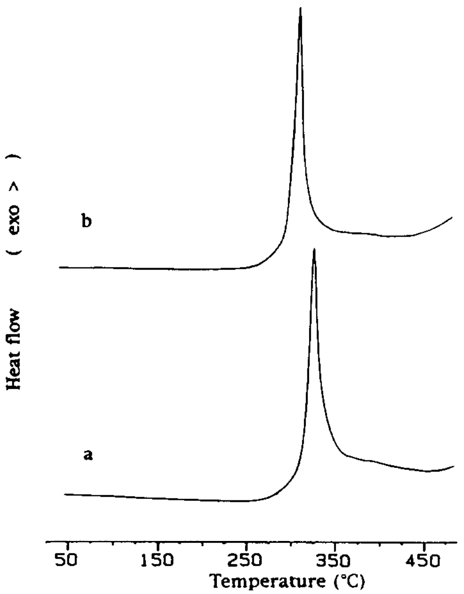

Fig. 7. DSC curves of PAN fibres in air flow. Heating rate: (a) 20°C min^{-1}; (b) 10°C min^{-1}.

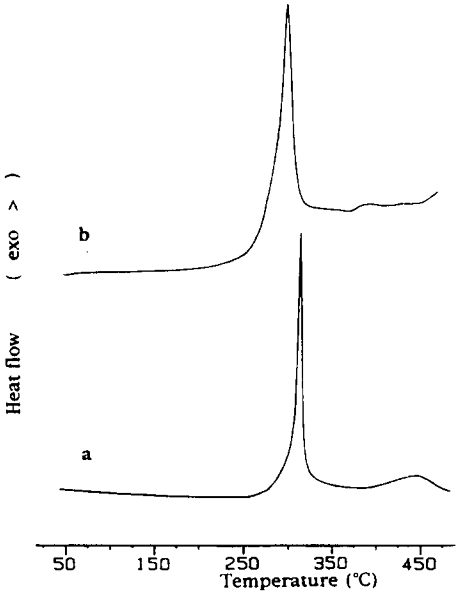

Fig. 8. DSC curves of AN–MA fibres in air flow. Heating rate: (a) 20°C min^{-1}; (b) 10°C min^{-1}.

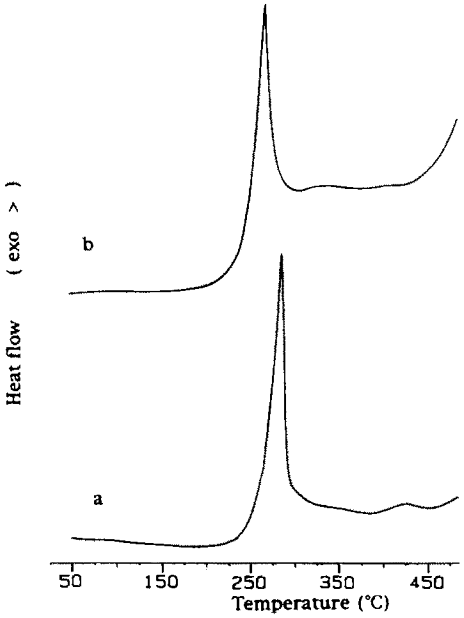

Fig. 9. DSC curves of AN–MA–IA fibres in air flow. Heating rate: (a) 20°C min^{-1}; (b) 10°C min^{-1}.

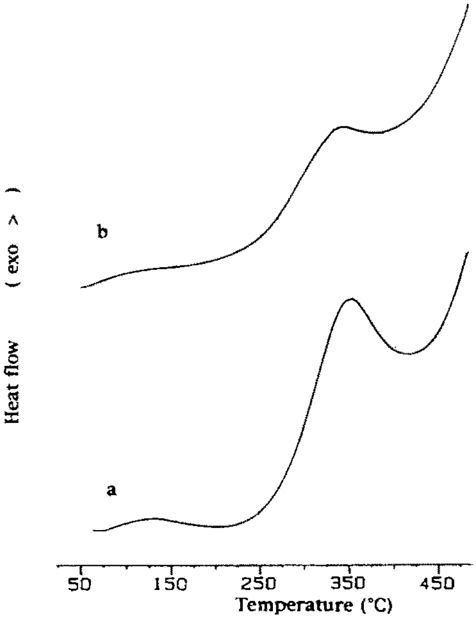

Fig. 10. DSC curves of Oxid. PAN fibres in air flow. Heating rate: (a) 20°C min^{-1}; (b) 10°C min^{-1}.

reaction is caused by the previous thermal stabilization below 300°C, which leads to a chemical modification due to cyclization reactions and to the partial oxidation of some functional groups of the macromolecules. In this case as well, the heat evolved during the main exothermic reaction is higher in air flow. During the calorimetric scan, at about 400°C and only under air, a new oxidative exothermic reaction begins.

Similar studies have been carried out by scanning at a 10°C min^{-1} heating rate (Figs. 3(b)–6(b) and Figs. 7(b)–10(b)), and the respective T_o, T_p and ΔH values are reported in Table 3. For all the acrylic fibres under study, both in N_2 and in air flow, the peak of the characteristic exothermic effect is lower in both T_o and T_p than the respective values obtained at a 20°C min^{-1} heating rate. The heat of reaction increases at the lower heating rate for the acrylic fibres. Other authors have reported [5, 6] that, for acrylic polymers, fragmentation phenomena in molecular chains are less important at lower heating rates; therefore, the endothermic contribution to the total amount of ΔH is lower.

The remarkable relative increase of ΔH, observed for PAN fibre at lower heating rates, as well as the above-mentioned smaller contribution to the fragmentation process, may be the result of microstructural characteristics. In fact, the SEM morphological study of this fibre shows a more even surface than the other fibres. This may be attributed to a larger diffusive control at the higher heating rate due to the large amount of gas, produced by the thermal decomposition.

For the Oxid. PAN fibre under air, the characteristic heat of reaction does not vary significantly when the heating rate changes.

The FT-IR spectrum of the PAN fibres (Fig. 11) shows the typical absorption of the polyacrylonitrile [5, 8] as well as some bands at 1736 and 1636 cm^{-1}; the latter persists after the drying at 80°C and is probably due to a functional group formed after the thermo-mechanical treatment (warm stretch) that the fibre might have undergone between 100 and 200°C [5, 7]. The weak band at 1736 cm^{-1}, typical of the stretching of the carbonyl group

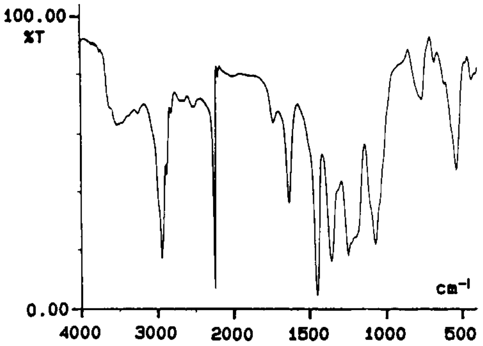

Fig. 11. FT-IR spectrum of PAN fibres.

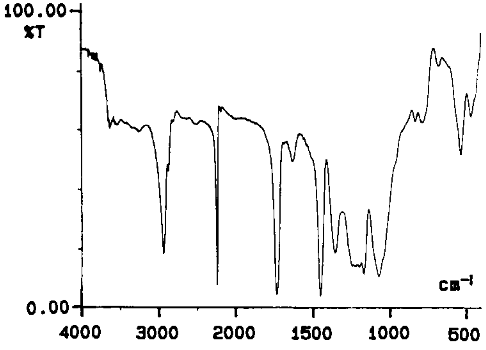

Fig. 12. FT–IR spectrum of AN–MA fibres.

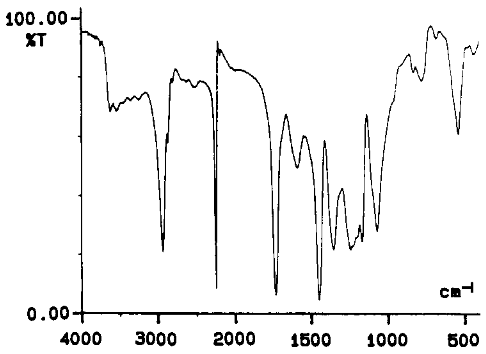

Fig. 13. FT–IR spectrum of AN–MA–IA fibres.

$\nu(C{=}O)$, might also be due to partial thermo-oxidation reactions of the nitrile group.

The FT–IR spectra of the two fibres from the copolymer (Figs. 12 and 13) show absorptions similar to those reported in the literature [9–11] for the acrylonitrile–methyl acrylate copolymer; moreover, for the AN–MA–IA fibre, a new medium intensity band, clearly visible in Fig. 13, is present in the 1592 cm^{-1} region, characteristic of conjugated structures; this might also be linked to a modification resulting from a thermo-mechanical process in the formation of the fibre. Weak bands, typical of the water absorbed by the fibres, are present in all the spectra in the 3621–3256 cm^{-1} range and at 1630 cm^{-1}. The Oxid. PAN fibre is mainly opaque to infrared rays; a very weak band at 2241 cm^{-1} shows a residue of the nitrile groups in the pre-oxidized fibre.

CONCLUSIONS

The analytical techniques used, DSC and FT–IR, can give useful information about the chemical and physical characteristics of fibres derived from acrylic polymers. Therefore, it is believed that possible interactions between fibres and cementitious matrix may be shown by modifications to the DSC characteristics and to the FT–IR spectra. Furthermore, it is also believed that SEM observations may indicate morphological variations associated with these interactions and thus be very helpful in understanding the phenomena.

To this end, all the fibres under study were added to mortar and concrete samples, now kept under controlled conditions. As soon as long periods of aging have been reached, their examination will be the subject of a future study.

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