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EXTRACTION AND IDENTIFICATION OF ORGANIC FIBRES FROM FIBRE-REINFORCED CEMENT COMPOSITES WITHOUT ASBESTOS

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ABSTRACT

Differential scanning calorimetry (1,2) is a very easy tool to use for the identification of blended organic fibres in cement composites. It necessitates the careful extraction of fibres from an inorganic matrix after treatment with a dilute formic acid solution.

The selective extraction and quantitative analysis of fibres is realized with specific solvents : isododecane for polyethylene, dimethylformamide for polyacrylonitrile and Schweitzer's reagent for cellulosic fibres.

Introduction

Many studies have been developed to substitute asbestos fibres in the fibre - reinforced cement (FRC) industry (3-7). Asbestos, which presents serious health hazards to workers when it is not used in adequate conditions, has been prohibited in some countries (8).

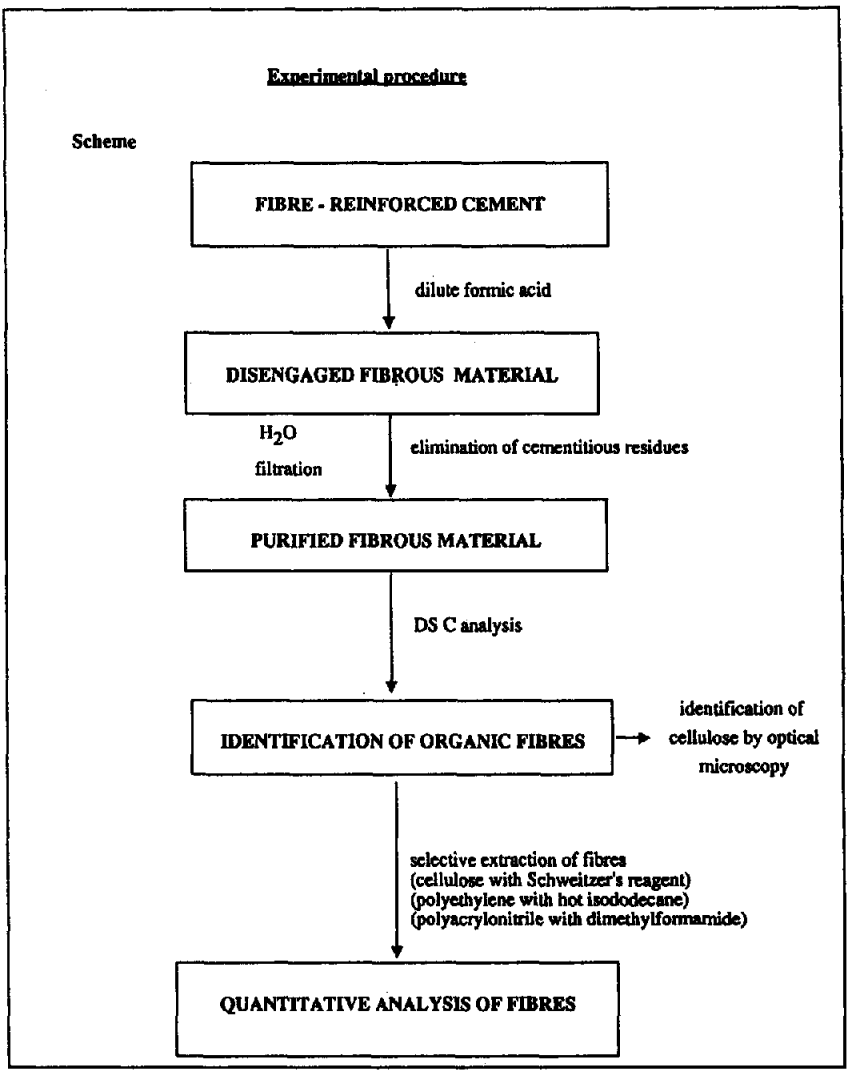
The most frequently used fibres include organic (acrylic, polyvinylalcohol, polyolefin), natural cellulose (9-12) (pulps from hardwoods and softwoods), inorganic (alkali - resistant glass, carbon) (13-16) and sometimes, polyethylene polypropylene copolymers.

Most of the fibre - reinforced cement composites (slates, corrugated sheets) use the above types of fibres : the cellulose for its availability and compatibility with the so-called Hatschek process, the polyolefinic synthetic pulps for their retention of fillers which aid their processing and properties and polyvinylalcohol (PVA) or polyacrylonitrile (PAN) for their outstanding mechanical properties.

The chemist needs to have easy and rapid methods to qualitatively and quantitatively analyze the amounts of these fibres.

In this paper, we describe a step by step procedure to recover the fibres without loss and also describe their analysis by differential scanning calorimetry (DSC) and their selective extraction from the blend.

The CLARK classifier is another method by which it is possible to separate the fibres according to their length and to obtain more information about their type. In particular, the origin



and treatment of the cellulosic fibres can be accurately assessed using colorimetric methods, following their separation from the other fibres.

Experimental

Obtention of Fibres. The materials tested were commercially produced fibre-cement composites. Flat or corrugated sheets of cementitious products (50 to 80g) were put into contact with dilute formic acid (250ml) at room temperature. The hydraulic matrix progressively disintegrated and the fibres were recovered with some binded cement particles by evenly scraping the material.

Grinding of the Fibrous Mat. The fibrous blend was dried in an oven at 105°C for 18 hours. Then, it was ground with a WILLEY mill (grid number 40, opening 40mesh) to obtain a powder which was subsequently homogenized in a Turbula homogenizer.

Ashes of the Fibrous Mat. The quantity of volatile organic components (VOC) was measured according to the following procedure. The fibrous mat, put in a crucible, was left for ten minutes without oxygen in an oven at 500°C and then for thirty minutes in the presence of oxygen (rate unmeasured). The mass of organic fibres in the finished product was determined by weighing the grey residue which remained in the crucible.

Measure of the Total Quantity of Organic Fibres in the Dry Mix of the Raw Materials. For manufacturing purposes, it is important to know the percentage of fibres in the dry mix of raw materials.

During its manufacture and cure, a fibre-reinforced cement composite usually undergoes hydration. We must take into account the fire loss of the cement composite, after 2 hours at 1000°C, for the calculation of the ratio of organic fibres in the initial dry mix (called A).

$$A = \frac{\text{fibres (\%)} \times 100 \text{ in the finished product}}{100 - [\text{fire loss (\%)} - \text{fibres (\%)}]}$$

Identification of Organic Fibres by Differential Scanning Calorimetry. The main types of cellulosic and organic fibres which are used as substitutes for asbestos are largely described in the literature (17,18). They are:

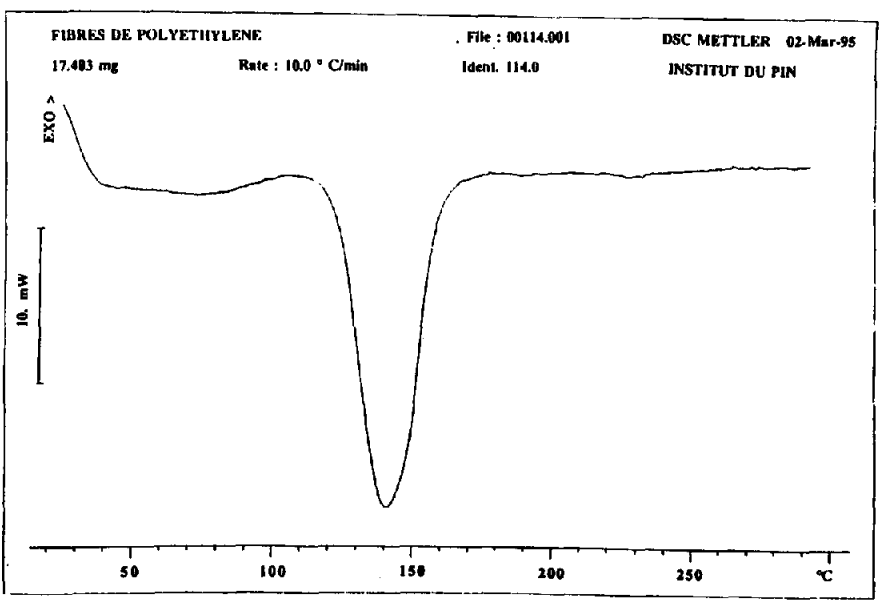


FIG. 1.
DSC diagram of PEhd fibres.

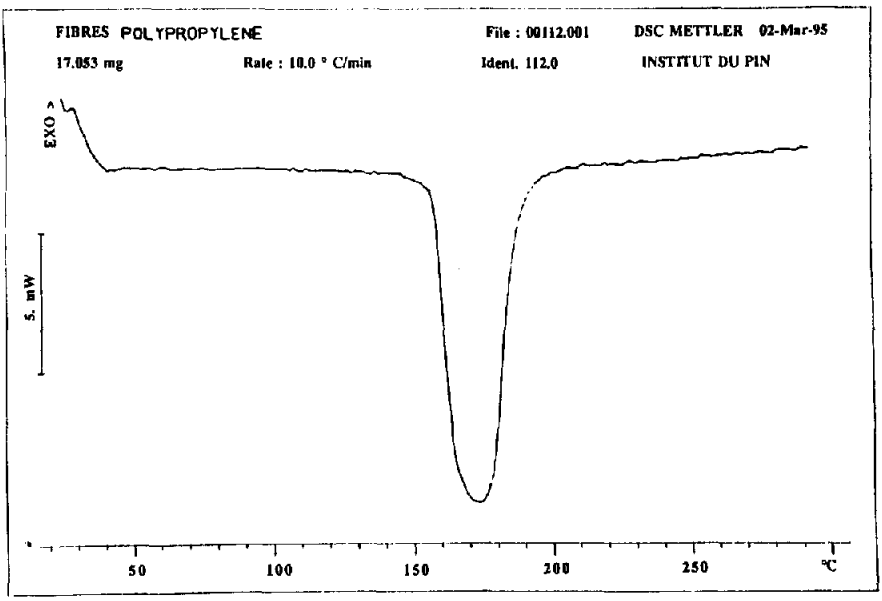


FIG. 2.
DSC diagram of polypropylene fibres.

*** cellulosic**

- unbleached and bleached pulps (harwoods and softwoods).
- mechanical and thermomechanical pulp.
- recycled old papers.
- vegetable fibres (flax - hemp - sisal - linter of cotton).

*** synthetic**

- acrylic (acrylonitrile).
- polyvinylalcohol.
- polyolefin pulps, polyethylene, polypropylene and comonomers.

DSC analysis was performed using a Mettler TA 3000 on 20-30mg of fibres, previously carefully dried under vacuum. The conditions were as follows:

- temperature range: 50 to 350°C.
- temperature rate: 10°C mn^{-1}.
- atmosphere: inert (N_2).

Results

Figures 1-4 represent the melting endotherms or exotherms obtained by the DSC of synthetic fibres (polyethylene - polypropylene - polyacrylonitrile, polyvinylalcohol) and the figures 5-6 represent the DSC plots of blended fibres (cellulose - polyethylene high density fibrillated pulp-polyacrylonitrile and cellulose - high density polyethylene fibrillated pulp - polyvinylalcohol).

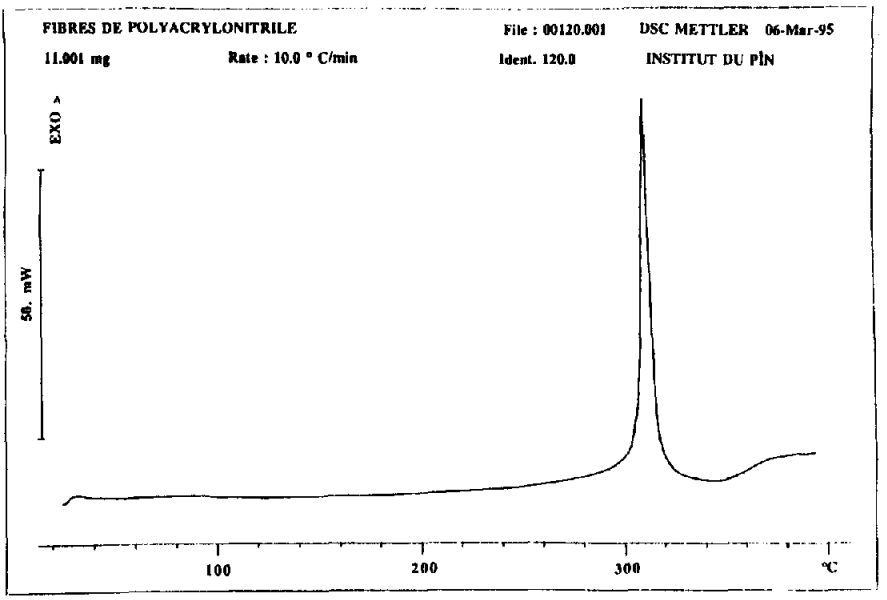


FIG. 3.
DSC diagram of polyacrylonitrile fibres.

The cellulosic fibres are characterized by an endotherm (peak: 100 - 150°C) which represents the internal self - dehydration of cellulose and two endotherms at 340°C and 360°C. The last one is characteristic of the decomposition of glycosidic linkages which result in the formation of gases which recombine exothermically.

Polyacrylonitrile fibres (DOLANIT from HOECHST - RICEM from MONTEFIBRE) show a characteristic exothermic peak at around 290-300°C. High - modulus polyvinylalcohol fibres (KURALON from KURARAY, MEWLON from UNITIKA) show an endotherm at 245-250°C (fusion of the polymer) and another endotherm at 360-365°C, which is analogous with that of cellulose (beginning of decomposition of the product).

Polyolefinic pulps show an endotherm at 135°C for high-density polyethylene and at 160-165°C for polypropylene.

Quantitative Analysis of Organic Fibres. This method was applied for FRC containing two or more fibres to obtain quantitative data. In this case, a blend of four fibres was choosen including cellulose, polyethylene, polyacrylonitrile and polyvinylalcohol fibres.

Dissolution of Cellulose Fibres Using Schweitzer's Reagent

Procedure. This reagent was prepared from copper hydroxide by using aqueous ammonia. The moist fibrous blend was introduced in a vial containing 200ml of Schweitzer's liquor and the suspension was maintained at 40-45°C in a water-bath during 30 minutes (this operation was realized under a well-ventilated hood). The suspension was filtered through a metallic wire

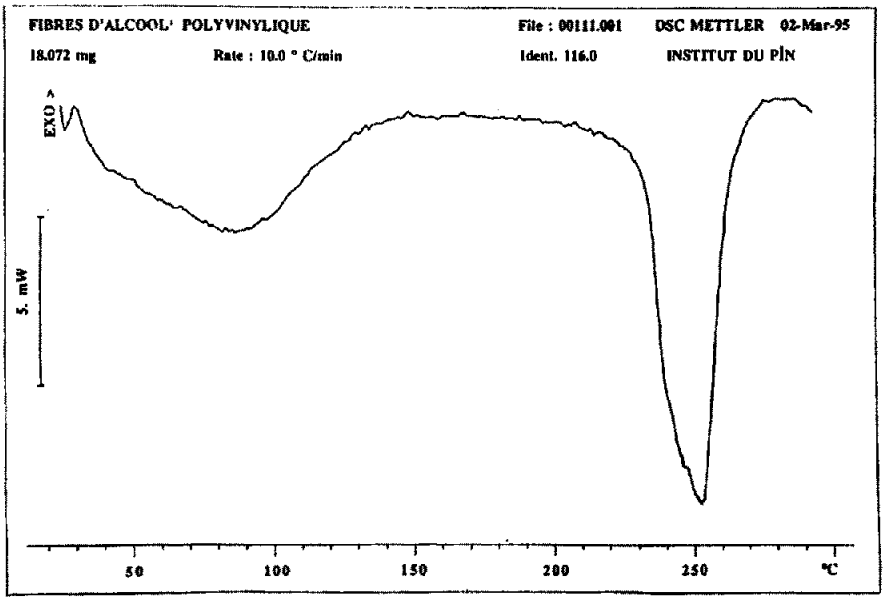


FIG. 4.
DSC diagram for polyvinylalcohol fibres.

sieve, then successively washed with 28% ammonia and then with water.The fibrous material was submitted to a second extraction and was dried in a ventilated oven overnight.

Results

The disappearance of the cellulose from the fibrous blend was confirmed by optical microscopy and DSC analysis. The cellulose, which is very easily coloured with specific dyes (De Graaf, Selleger, Herzberg) and shows caracteristic profiles of hardwoods or softwoods fibres is totally absent form the remaining fibres. The endotherm at 100-150°C is suppressed on DSC plots.

Dissolution of Polyolefinic Fibres

Procedure. The remaining blended fibres were introduced into a flask containing 200ml of isododecane at 130°C and stirred for 15 minutes.

The suspension was filtered and then washed with hot isododecane. A similar second extraction was realized. The remaining fibres (PVA and PAN) were washed with acetone to eliminate traces of solvent, then dried overnight in an oven at 105°C. The weight of PVA and PAN was then determined.

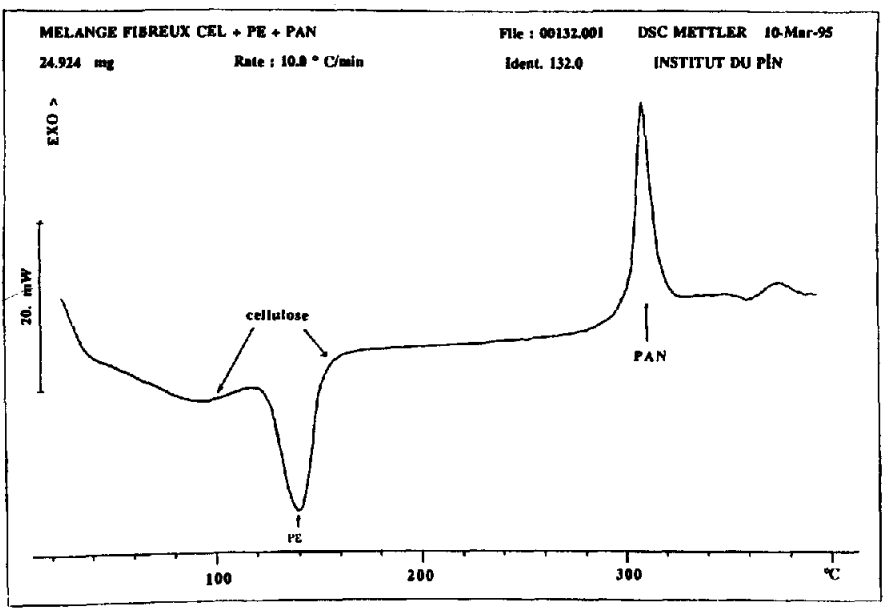


FIG. 5.
Representative diagram of fibrous material with cellulose, PEhd and polyacrylonitrile fibres (from slate).

Results

The precipitate of polyethylene was recovered from the isododecane solution whose temperature was maintened overnight at 0°C, washed with acetone and dried at 105°C.

The total extraction of polyethylene fibres was confirmed by DSC analysis of the remaining fibres (no melting endotherm was observed at 135°C) and by optical microscopy (the polyethylene fibers which appear as black coloured flakes with Selleger dye were absent).

Dissolution of Polacrylonitrile Fibres. After the removal of polyethylene fibres, it was necessary to separate PVA fibres from PAN fibres. This is done using dimethylformamide (DMF) which is a solvent of the PAN fibres. The residue constitutes of PVA fibres which were weighed.

Conclusions

We have developed an easy-to-use method for the determination of organic fibres in cementitious products used in the building industry. The recovery of organic fibres is made possible with the disintegration of the cement matrix using a formic acid solution and does not result in the decomposition of fibres. The DSC analysis of the disengaged fibrous material gives the different types of organic fibres.

The cellulosic fibres can be identified by coloration when using specific dyes. The Herzberg dye fives hardwoods fibres a blue coloration while it gives those of softwoods a brownish colour. The use of selective solvents gives the quantitative percentages of each organic fibre with reproductible results.

Acknowledgements

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