Original Papers

HIGH-TEMPERATURE DILATOMETRY OF FIBRE REINFORCED CALCIUM HYDROSILICATES

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By the method of high-temperature dilatometry were studied the properties of thermal insulating materials on the basis of a calcium hydrosilicate binder and fibrous microreinforcement. New fibre types for the replacement of asbestos can influence negatively the hydrothermal hardening of the binder. The shrinkage values upon the burning out of cellulose fibres are negligeable in comparison with the shrinkage growth at a lower degree of the crystalline development of the binder. On the basis of dilatometric data from the high-temperature dilatometer NETZSCH – 402 E, processed on the HP 9820 A computer, was carried out a selection of suitable cellulose fibre types and the temperature interval of the application of the prepared materials was defined. High-temperature dilatometry seems to give more informations about calcium hydrosilicate matrix of composites than XRD and SEM methods.

INTRODUCTION

High-temperature dilatometry has become an indispensable method for assessing the quality of fibrous thermal insultating materials as well as their binder systems based on 11 Å-tobermorite and xonotlite [1, 2, 3, 4, 5]. Recently has been culminating the endeavour to replace asbestos microreinforcement with other fibres which, however, sometimes influence negatively the development of the binder system during the hydrothermal synthesis. The method of high-temperature dilatometry allows already on model systems the selection of suitable cellulose fibre types for microreinforcement, as well as the definition of a temperature interval for the application of the prepared materials.

EXPERIMENTAL

Model systems of the calcium hydrosilicate binder and fibrous microreinforcement were prepared in a starting molar ratio $CaO / SiO_2 = 1.0$ from Ca● a.r. grade, SiO_2 – dust from the manufacture of silicon in Mníšek pod Brdy (97.27 % SiO_2) and 4–10 % fibrous materials (related to the solid phase) of a cellulose character. Three types of cellulose were employed: microcrystalline, semi-chemical and waste – knot material. The hydrothermal processing takes place in cylindrical stainless stell autoclaves with a volume of 45 ml at a filling of 30 ml of a water suspension of the raw materials and a verified hydrothermal reaction mode with a prereaction (95°C / 2.5 h + 193°C / 5 h) [6, 7]. In the initial phases of the reaction the entire volume is mixed periodically and after the hydrothermal reaction in the horizontal position of the autoclaves the resultant product is a composite element in the form of a cylindrical segment, from which are cut after drying measuring beams 5 × 5 × 35 mm for dilatometry.

Measurements of dilatation changes were carried out on the high-temperature dilatometer NETZSCH – 402 E upon heating up to 1000°C and heating rate of 5°C / min with the recording of data on a two-channel recorder. The determined values were processed on the HEWLETT PACKARD 9820 A computer and drawing equipment 9862 A [8]. At the present time is also employed HEWLETT PACKARD equipment for data acquisition and processing in the following configuration: desk-top computer HP 85 F with 32K RAM – multiplexer scanner 3495 A - digital voltmeter 3455 A - plotter 7470 A - printer 82905 A.

The mineralogical composition and degree of crystalline development of the internal structure of the binding phases were determined by X-ray methods on the APD 15 instrument of PHILIPS.

The microstructure of the composites and the morphology of the binder components as well as the fibrous microreinforcement were studied with the aid of the STEREOSCAN 2A scanning electron microscope of CAMBRIDGE.

RESULTS AND DISCUSSION

The fundamental calcium hydrosilicate binder of the xonotlite type exhibits upon heating soundness

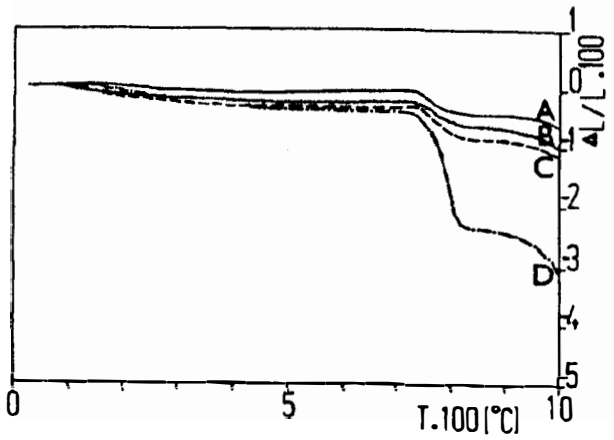

Fig. 1. High-temp. dilatation curves of xonotlite matrix (A) and composites with microcryst. cellulose (B), waste-knot cellulose (C) and semi-chemical cellulose (D).

up to a temperature of 730°C, when there begins a transformation of xonotlite onto wollastonite [9], accompanied by shrinkage to the value –0.5 % at 800°C. A further gradual shrinkage occurs after the exceeding of 930°C (Fig. 1, curve A).

4 % of microcrystalline cellulose in the composite manifest themselves by a shrinkage of the value –0.25 % at 350°C, caused by the burning out of organic components. Upon a further temperature increase the system behaves in a similar way as the pure binder, with a shrinkage value of –0.75 % at 800°C and a further bend of the curve shifted to 900°C (Fig. 1, curve B).

4 % waste knot cellulose in the system causes by burning out up to 350°C a shrinkage of the value –0.35 %. The further slope of the dilatation curve is analogical to the binder curve and attains the value of –0.9 % at 800°C with a subsequent bend at 900°C (Fig. 1, curve C).

4 % of semi-chemical cellulose in the composite system also burn out up to 350°C and cause shrinkage with a value of –0.35 % which as a plateau attains 730°C, when there begins a transformation of the binder into wollastonite terminated at 830°C with a shrinkage to the value –2.4 %.After exceeding 900°C there occurs a further bend of the curve as in the previous cases (Fig. 1, curve D). The determined shrinkage value of –2 % in the phase transformation region of xonotlite onto wollastonite represents four times the values for the pure binder component as well as the previous two composite systems. There can thus be assumed a certain influencing of the crystalline development of the internal xonotlite structure by fibres of semi-chemical cellulose.

By an X-ray analysis of the four investigated systems was unambiguously proved the identical character of their binder component formed by xonotlite with a high degree of crystalline development of its internal structure.

Also during the study of the structure of composites with the scanning electron microscope was confirmed the identical character of the binder morphology in all four systems. The morphology of xonotlite with a high degree of crystalline development of its internal structure is depicted by an SEM in Fig. 2. Wollastonite prepared from xonotlite at 1 000°C/ 4 h is morphologically very close to the starting phase – SEM Fig. 3. In the xonotlite matrix of composites with microcrystalline cellulose – SEM Fig. 4 – as well as semi-chemical cellulose – SEM Fig. 5 – can readily be seen xonotlite crystals which are morphologically identical with the pure binder phase.

CONCLUSION

High-temperature dilatometry is suitable for the rapid and practical determination of the thermal and technical parameters of insulating materials with a fibrous microreinforcement.

Cellulose fibres increase slightly upon burning out the shrinkage value of a composite with a xonotlite matrix.

Based on dilatometric measurements we can hypothesize that microcrystalline and waste (knot material) cellulose do not influence the synthesis of the main binder component of the xonotlite matrix and semi-chemical cellulose acts lightly negatively onto the crystalline development of xonotlive with a subsequent increase of the shrinkage value of the composite in the area of the phase transformation of the binder onto wollastonite which, however, cannot be determined by X-ray methods and not even with the aid morphological SEM's from the scanning electron microscope. High-temperature dilatometry seems to give more informations about calcium hydrosilicate matrix of composites than XRD and SEM methods.

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VYSOKOTEPLOTNÍ DILATOMETRIE VÁPENATÝCH HYDROSILIKÁTŮ VYZTUŽENÝCH VLÁKNY

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Vysokoteplotní dilatometrie byla užita ke studiu vlastností tepelně izolačních materiálů složených z vápenatokřemičitého pojiva a vláknité mikrovýztuže. Nové typy vláken pro náhradu azbestu však mohou negativně ovlivnit proces hydrotermálního vytvrzení pojiva v kompozitu. Hodnoty smrštění při vyhořívání celulosových vláken v průběhu záhřevu kompozitu jsou zanedbatelné ve srovnání se smršťováním způsobeným nižším stupněm krystalického vývoje pojivových fází v matrici. Na základě dilatometrických dat z vysokoteplotního dilatometru NETZSCH – 402 E byl proveden výběr vhodných celulosových vláken pro kompozitní materiál včetně stanovení teplotního intervalu pro jeho použití. Vysokoteplotní dilatometrie poskytuje při studiu kompozitů více informací o vápenatokřemičitém pojivu než metody XRD a SEM.

Obr. 1. Křivky vysokoteplotní dilatace xonotlitové matrice (A) a kompozitů s mikrokrystalickou celulosou (B), sukovinou-odpadní celulosou (C) a polo-chemickou celulosou (D).
Obr. 2. SEM xonotlitové matrice.
Obr. 3. SEM wollastonitu připraveného z xonotlitu při 1000° C/4h.
Obr. 4. SEM kompozitu s mikrokrystalickou celulosou.
Obr. 5. SEM kompozitu s polo-chemickou celulosou.

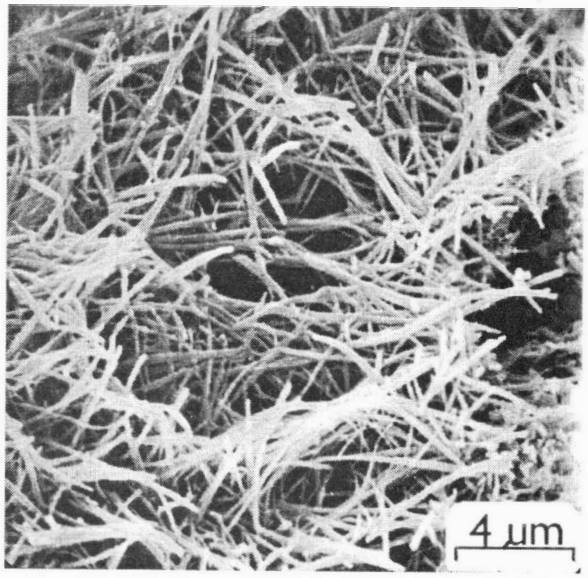

Fig. 2. SEM of xonotlite matrix

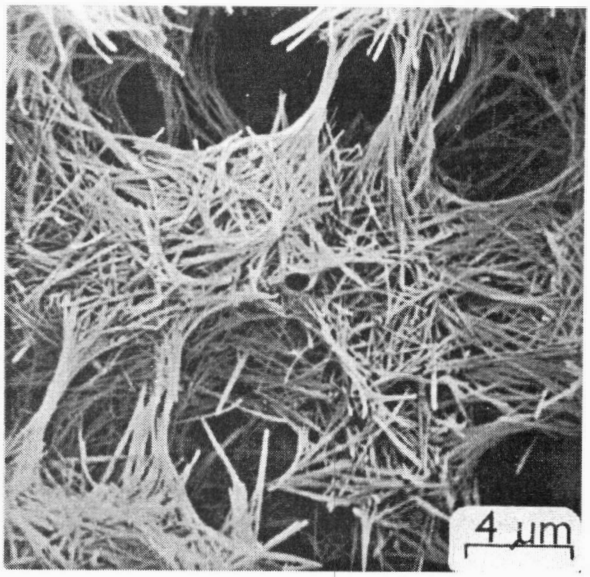

Fig. 3. SEM of wollastonite prepared from xonotlite at 1000 °C/4h.

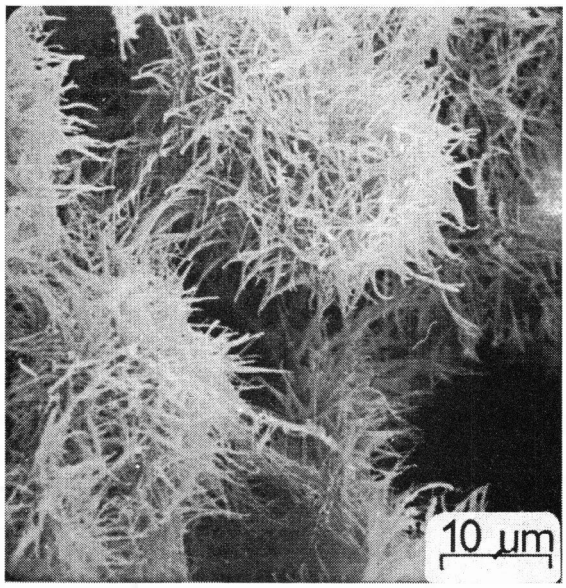

Fig. 4. SEM of composite with microcrystaline cellulose.

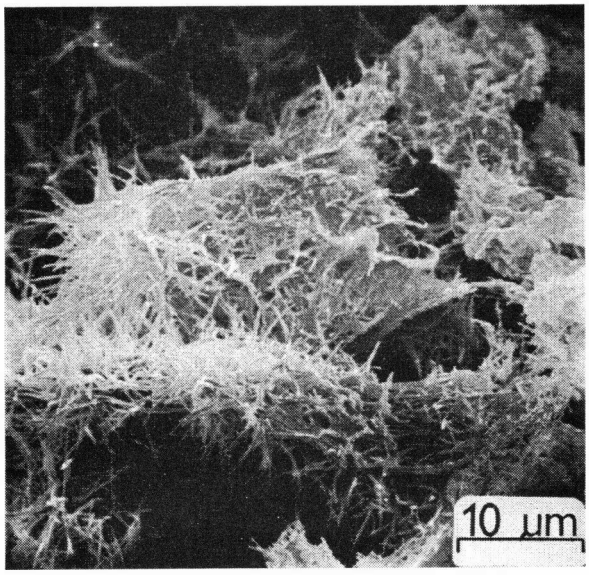

Fig. 5. SEM of composite with semi-chemical cellulose.