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RAMAN SPECTROSCOPY STUDY OF INTERFACIAL TRANSITION ZONE IN CEMENT COMPOSITE REINFORCED BY PP/PE AND BASALT FIBRES

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ABSTRACT
The structural changes of interfacial transition zone of two concrete systems reinforced by polypropylene/polyethylene and basalt fibers were studied by Raman microspectroscopy. The interfacial transition zone was found in the 0-20 μm in vicinity of quartz/feldspar aggregate surface. The calcium carbonate, ettringite and alite and belite bands were used for determination of interfacional transition zone size by Raman spectroscopy. Similar behaviour has been shown the cement matrix in neighbourhood of PP/PE fibers. There is not observed any concentration gradient of cement hydration product in the vicinity of 1 μm diameter basalt fiber.

KEYWORDS: Raman spectroscopy, cement composite, interfacial transition zone, polymer fibers, basalt fibers

Cement-based materials, such as Portland cement pastes, mortars and concretes are brittle in nature, with a high compressive strength and a low tensile strength and toughness. Therefore, the use of these materials in practice involves their combination with reinforcing, either with steel rods in convential reinforced concrete, or with fibers in special components of fiber reinforced cements and concretes.

Different fiber types with various properties can be used for cement reinforcement (Bentur and Midness, 1990; Balagru and Shah ,1992). In general, fibers made of a high-strength, high-modulus material, such as glass, carbon, aramid and high density polyethylene, will usually increase the strength and toughness of the cement composite. In case of low-modulus material, such as polypropylene and polyethylene, the reinforcement enhance mainly the ductility of the cement composite, but not its strength, resulting in strain softening or elastic-plastic behavior.

It is widely accepted that the mechanical behaviour of polymer composites is highly dependent on the interphase between the fiber and the matrix. This interfacial transition zone interphase exists at some area around the fibre surface, where the local properties including the morfological features, chemical compositions and thermo-mechanical properties begin to change from the bulk matrix properties (Drzal, 1986; Kim and Mai, 1998). The range of the microstructure and mechanical property gradients within the interphase is from nanometers to micrometers. Both a monotonic decrease of the interphase modulus in comparison with the matrix modulus (Theocaris, 1985) and the gradient modulus along interphase (Sottos et al., 1992) have been proposed. Several different test methods, such as the Raman spectroscopy stress field analysis (Bannister et al., 1995) and the nanoindentation test (Hodzic et al., 2000) were used to investigate the interphase properties.

The microstructure of the paste matrix in the vicinity of the transition zone of the fibers is considerably different from that of the bulk paste away from the interface (Bentur and Midness, 1990; Olivier et al., 1995). The microstructure of the transition zone with monofilament fibers has been studied primarily in a steel fiber reinforced paste (Balagru and Shah, 1992).

It was observed that the transition zone in the mature composite is rich in $Ca(OH)_2$, usually in direct contact with fiber surface, and is also quite porous, making it different from the microstructure of the bulk paste. The $Ca(OH)_2$ layer is about 1 μm thick (Peled and Bentur, 2000) and resembles the duplex film suggested by Barnes et al. (Peled et al., 1992). Peled et al. (1998) studied the bond performance mono-filament polyethylene yarns embedded in a cement matrix to resolve yarn-matrix interaction mechanism. Pull-out tests were carried out for mechanical characterization of the bonding. It was found that the pul-out resistance of the straight yarn was controlled by frictional as well as anchoring effects.

The main spectroscopies employed to detect vibrations in molecules are based on the processes of infrared absorption and Raman scattering. They are widely used to provide information on chemical structures and physical forms, to identify substances from the characteristic spectral patterns, and to determine quantitatively or semi-quantitatively the amount of a substance in a sample.

The aim of this paper is to describe of structrural changes of interfacial transition zone of two concrete systems reinforced by polypropylene/polyethylene and basalt fibers by Raman microspectroscopy.

EXPERIMENTAL

Mixture of Quick-setting Portland cement CI52,5 Rohožník (24 weight parts), sand 0/4 Hostim (34 weight parts), aggregates Hostim 4/8 (35 weight parts, cement plastificator Re18 fy HaBes (0.25 weight parts)were used. Polypropylene/polyethylene fibres BeneSteel 50 µm x 35 µm x 50 mm or basalt fibres (Kamenyj Vek, R) of 1 µm diameters and 50 mm length were added at in quantities 1% related to cement.

Raman spectra were collected using the LabRam system Jobin Yvon model Labram HR equipped with the 532 nm line laser was used for excitation of cement materials and 785 nm for polymer fibres. The objective (×100) was used to focus the laser beam on the sample placed on an X-Y motorized sample stage. The scattered light was analyzed by spectrograph with holographic grating (600 gr/mm), slit width 100 µm and opened confocal hole (1000 µm). The adjustment of the system was regularly checked using a silicon sample and by measurement in the zero-order position of the grating. The time of acquisition of a particular spectral window was optimized for individual sample measurements (ca. 20 - 100 s). Twenty acumulations were co-added to obtain a spectrum.

RESULTS

In Fig. 1 is presented photography of analyzed concrete reinforced by PP/PE fibres. Analyzed area, dimension 100 x 140 µm is shown in Fig. 2. The spectra of particular concrete components, thus aggregate, cement matrix and fibres were measured in analyzed area.

The spectra of cement matrix in dependence on distance from edge of aggregate were collected too. It was found the aggregate is created by quartz/feldspar as evident from the dominant bands at 464 and 512 cm^{-1} in its Raman spectrum (see Fig. 3.). The bundle of polymeric fibres is created by polypropylen/polyethylen blend (50:50 weight parts). Spectra of

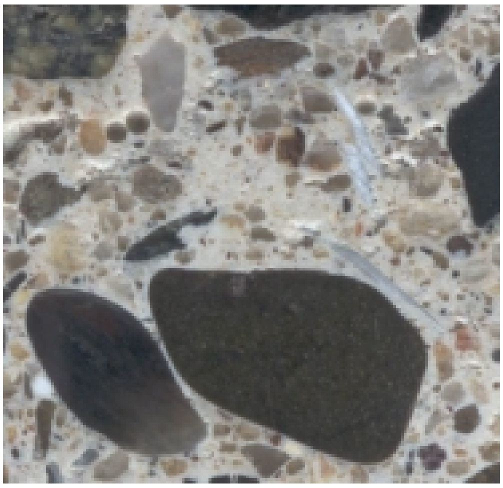

Fig. 1 Concrete reinforced by PP/PE fibres

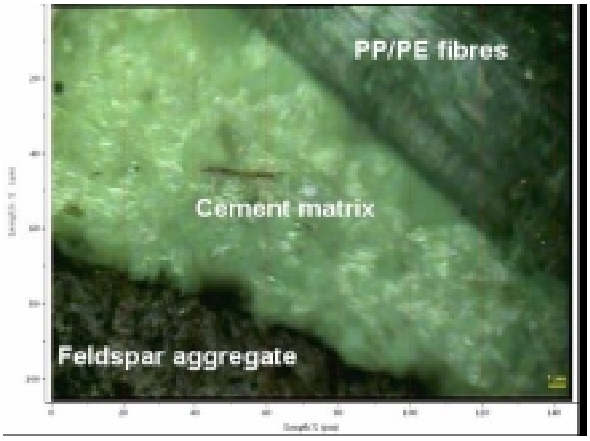

Fig. 2 Microphoto of concrete-PP/PE polymer analyzed area (magnification 10x)

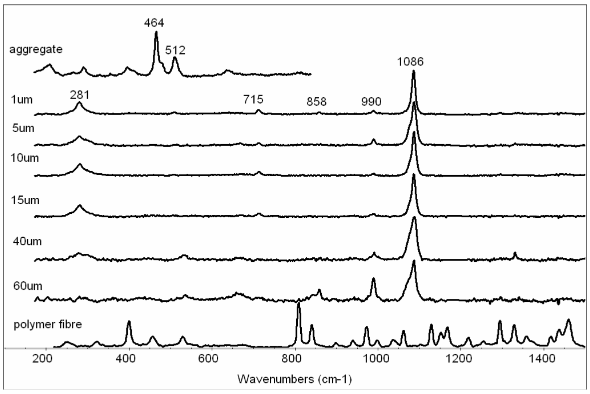

Fig. 3 Raman spectra of quartz/feldspar aggregate, cement matrix of various distances from quartz/feldspar aggregate surface and spectrum of PP/PE polymer

cement matrix measured at distance of 1, 5,1 0, 15, 40 and 60 μm from aggregate edge are also presented in Fig. 3.

Portland cement is a heterogeneous mixture of four main compounds with the approximate following composition: 50-70 % of tricalcium silicate (Ca_3SiO_5), 20-30 % of dicalcium silicate (Ca_2SiO_4), 5-12% tricalcium aluminate ($Ca_3A1_2O_6$), and 5-12% of calcium aluminoferrite ($Ca_4Al_2Fe_2O_{10}$). In cement chemistry these components are abbreviated as: C_3S (alite) for tricalcium silicate; C_2S (belite) for dicalcium silicate; C_3A for tricalcium aluminate andC_4AF for calcium aluminoferrite. The hydration of dry clinker leads to the formation of mainly: 20-25% of $Ca(OH)_2$ (portlandite, CH), 60-70% of $3CaO.2SiO_2.3H_2O$ (calcium-silicate-hydrate, C-S-H), and 5-15% of other solid phases e.g. ettringite $[Ca_6Al_2(SO_4)_3(OH)_{12} . 26H_2O]$.

Two significant bands of products of cement hydration at 1086 and at 990 cm^{-1} in Raman spectra with have been found. Band at 1086 cm^{-1} corresponds to calcium carbonate, which originated by secondary carbonation of calcium hydroxide owing to airy CO_2 on the specimens surface and from its intensity we can presume to primary concentration of $Ca(OH)_2$ in cementious matrix. Further bands of $CaCO_3$ with can be found at 715 and 281 cm^{-1}. The ettringite band can be seen at 990 cm^{-1}. The intensive bands in Raman spectra of principal cement compound alite and belite at 838 and 858 cm^{-1} have appeared.

In Raman spectrum of measuring point in distance of 60 μm from quartz/feldspar aggregate, we can see a relatively intensive band at 858 cm^{-1}, which coresponded to non-hydrated belite. For the semi-quantive estimation of cement matrix structure the intensity ratio of carbonate/C_2S and ettringite/C_2S bands has been used. Results are presented on Figs. 4 and 5.

From results is evident in vicinity of aggregate edge the so-called interfacial transition zone (ITZ) is presented in the region 5 - 20 μm from aggregate surface, maximal concentration of cement hydratation products thus $Ca(OH)_2$ and ettringite were detected. In bigger distance from the aggregate, behind interfacional zone, increase part of no-hydrated parent cement compounds as are alit, belite, C_3A and C_4AF we can found. The results correspond to ITZ conception described in literature (Oliiver et al., 1995). The geometrical arrangement of cement grains in water will be disturbed in concrete by the presence of aggregates. This involves a wall effect creating a gradient for water concentration in the cement paste and thus a W:C ratio gradient. It has a number of consequences on the microstructure of the hydrated cement paste in the vicinity of the aggregates. The relatively large dimension of the spaces remaining vacant for the formation of the first hydrates, together with the significant variations in mobility of ions. A locally greater W:C ratio with fewer nucleation sites results in a formation of larger, better-formed, and preferentially oriented crystals in contact with aggregates. Finally, as the pores to be filled in are larger, the porosity, at all ages, will remain higher. Thus, a zone where the paste has a microstructure different from the surrounding bulk exists around the aggregate particles. The microstructural characteristics of this zone vary gradually from the surface of the aggregates. The phenomenon therefore clearly involves an ITZ. The consequences of initial geometrical perturbation on the microstructure have in turn an effect on the properties of the ITZ, which is mechanically less resistant than the bulk. The first

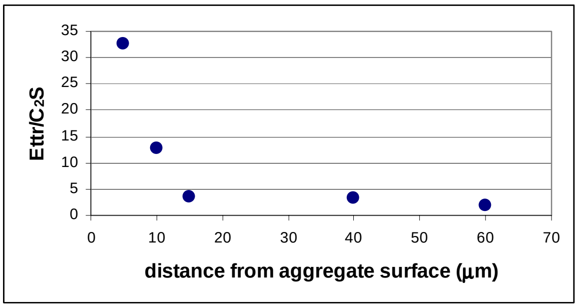

Fig. 4 Relative concentration of ettringite as a function of the distance from quartz/feldspar aggregate surface

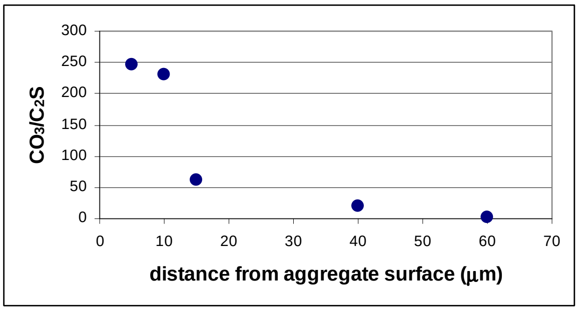

Fig. 5 Relative concentration of carbonate as a function of the distance from quartz/feldspar aggregate surface

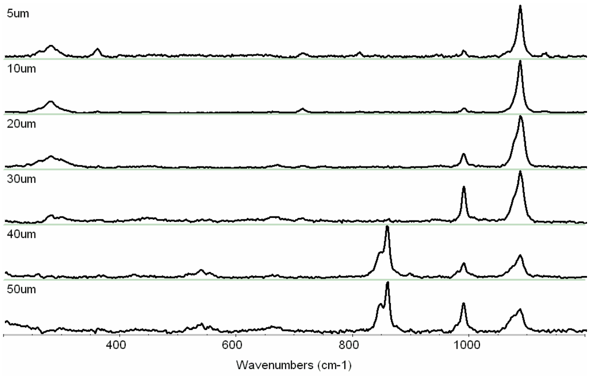

Fig. 6 Structure of cement matrix vs. edge distance of PP/PE fibres

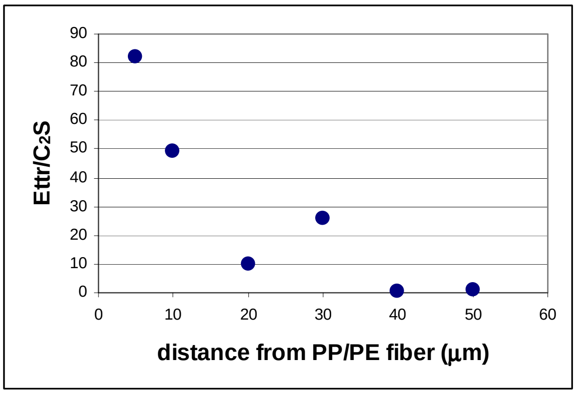

Fig. 7 Relative concentration of ettringite as a function of the distance from PP/PE fibre surface

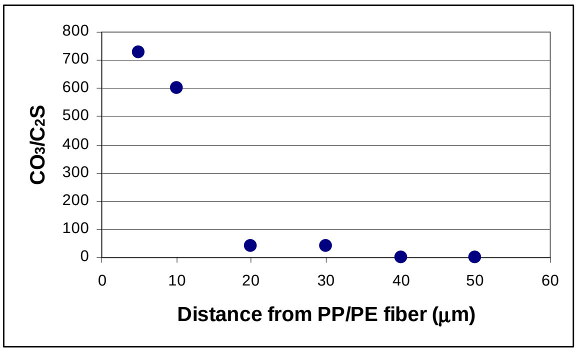

Fig. 8 Relative concentration of carbonate as a function of the distance from PP/PE fibre surface

microcracks resulting from mechanical or hygrothermal action will appear in this zone. The microstructural differences between the paste in the ITZ and that in the bulk will be lowered (Olivier, 1995).

In Figure 9 is presented analyzed area of concrete containing 1% of basalt fibers of diameter 1 µm and 5 cm of length. In Fig. 10 are shown Raman spectra of the original basalt glass fibre with bands at 503 and 940 cm^{-1}. Raman spectrum of basalt fibers immersed in hydrated cement matrix is presented in the same picture. Spectra of both fibers show no significant band shifts, which point to minimal structural changes of basalt fibers during hydratation of cement matrix. In the second spectrum the carbonate band at 1086 cm^{-1} is shown. In spectrum was also found band at 3600 cm^{-1} (spectrum not shown), which pertain to OH bonds of calcium hydroxide. This substance was not found in cement matrix in vicinity of fibers. Dependence of structure of cement matrix found by Raman spectroscopy in different distance from basalt fibers is introduced in Fig. 11. It is evident that no significant intensity changes of calcium carbonate and ettringite bands with distance from fiber are presented. In distance of 60 µm from fibre were not found of the surface cement matrix non-hydrated initial cement components as is e.g . alite and belite. It seems that in the vicinity of basalt fibres ITZ not occurs which is evidently due to geometrical arrangement of basalt fibers otherwise its chemical structure.

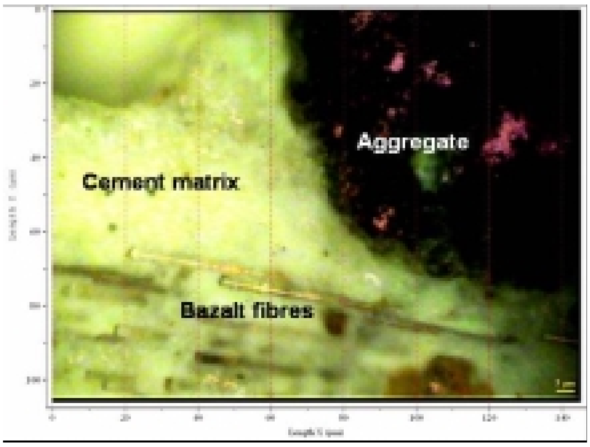

Fig. 9 Image of analyzed area (magnification 10x)

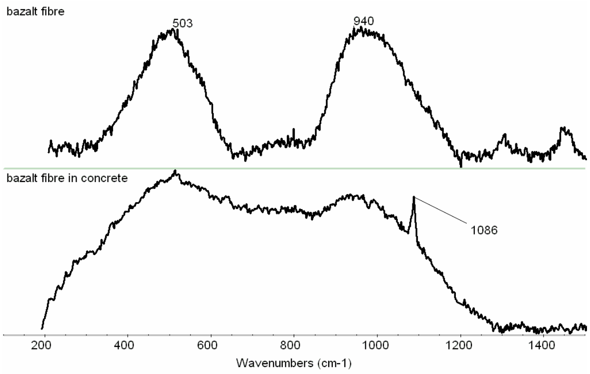

Fig. 10 Raman spectra of parent basalt fibre and the fibre deposited in cement matrix

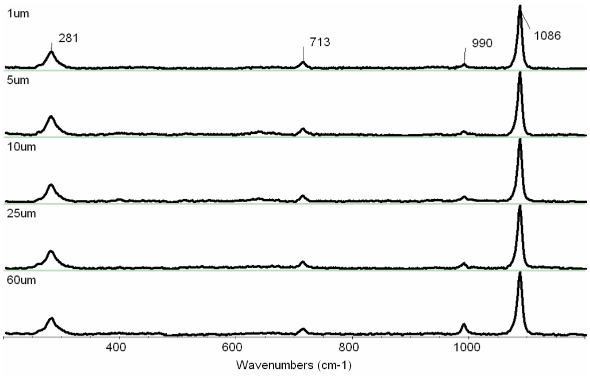

Fig. 11 Structure of cement matrix vs. edge distance of basalt fibres

CONCLUSION

In the paper were described the structrural changes of interfacial transition zone of two concrete systems reinforced by polypropylene/polyethylene and basalt fibers by Raman microspectroscopy. On the basis of calcium carbonate, ettringite, alite/belite band intensities the interfacial transition zone was found in the 0-20 μm region in vicinity of quartz/feldspar aggregate surface. Similar behaviour has been shown the cement matrix in neighbourhood of PP/PE fibers. On the other hand no transition zone was detected at the area close to basalt fibres surface. There is not presented any concentration gradient of cement hydratation products, which is evidently due to geometrical arrangement of basalt fibers otherwise its chemical structure.

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