



Concrete-like polymer composites with fly ashes – Comparative study

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HIGHLIGHTS

- ▶ Implementation of sustainable development in polymer concrete technology.
- ▶ Analysis of fly ashes usability for modification of polymer concretes.
- ▶ Proof of replacement of expensive filler by calcium fly ashes.
- ▶ Material model of fly ash polymer concretes useful for composition optimization.

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ABSTRACT

The modern trend of disposing industrial wastes and by-products into building materials that complies with the implementation of sustainable development enables reducing material cost of expensive composites materials, e.g. polymer concretes (PCs). The high material cost of polymer concretes is one of the main contraindications of their widespread use despite of their advantages – very good mechanical properties and high chemical resistance. The cost may be reduced by substituting expensive components with cheaper equivalents, including fly ashes, the by-products of coal combustion.

In the paper the results of studies concerning polymer concretes containing fly ashes were discussed. The polymer concretes contained fly ashes of various types, origin, combustion technology and chemical composition. The considered data were the results of studies available in literature as well as results of own research study. The influence of fly ash type and content on PC mechanical properties, such as compressive strength, flexural strength and tensile strength but also on chemical resistance were investigated and analyzed. Moreover fly ashes were compared against the material often applied as very fine-grained filler to concrete-like polymer composites, the raw substance – quartzite meal.

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1. Introduction

In the era of sustainable development the common trends are rationalizing the use of natural sources, energy and work and developing new pro-ecological technologies that enable reducing level of pollution, minimizing consumption of raw materials and on the other hand increasing the waste products recycling. For this reason much emphasis is placed on developing ways of disposing industrial by-products/wastes into building materials.

This approach well known from cement concrete technology where several recycled materials are applied (e.g. crushed concrete, recycled glass – as aggregate, fly ashes, paper meal ash – as very fine graded fillers, i.e. microfillers) is introduced also into polymer concretes. For instance, popular trend was applying recycled resins (e.g. thermoplastic resin from waste polyethylene tere-

phthalate [1]) into concrete, which enabled producing good quality PC at a relatively low cost. Nowadays, following the example of cement concrete technology, also fillers are being substituted.

2. Microfillers applied into concrete-like polymer composites

When figuring out the method of designing polymer concretes, including the qualitative and quantitative selection, few tendencies may be noticed. Czarnecki [2] as very fine graded fillers applied into polymer concrete listed most of all: milled stone materials – silica fume, quartzite meal, granite meal, andesite meal, calcium carbonate/lime powder and various cements (e.g. Portland cement applied to acrylic and epoxy concretes, aluminous cement – in polyester concretes). The application of coke and graphite, and asbestos dust [2,3], not permitted for use any more is mentioned. In the first decades of elaborating composites with polymer binders many tries were done to find the best components of PC. However, according to Czarnecki [2], the optimal microfiller for polymer concrete should be petrographically identical or

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comparable to its basic aggregate. After analysis of the interdependence of micro-fraction of aggregate and resin binder Czarnecki as the appropriate values of binder to microfiller ratio (B/M) indicates values from a range of 0.4 to 0.6.

Sung et al. [4] who investigated polyester concretes containing river aggregate and mix of silica powder and heavy calcium carbonate in different proportions as microfiller showed that the higher was the CaCO_3 content, the lower mechanical strength (compressive, flexural and tensile strength, dynamic modulus) concretes obtained.

In general, at nineties of the last century, adding calcium carbonate as a microfiller fraction into polymer concrete-like composites was a popular idea – except mentioned study of Sung et al. [4] – it was done e.g. by Rebeiz [5]; Soh et al. [6] who also compared influence of calcium carbonate and fly ash. On the other side Özkul [7] used Portland cement; others mixed various stone fillers of different grading (e.g. Voznensky et al. [8] used multi-fraction filler – the mix of andesite and silicon carbide in carbamide concrete). In the last decade popular microfiller of polymer concretes was silica powder/quartzite meal used among others by Garbacz and Garboczi [9], Golestaneh et al. [10], some researchers modified it with coupling agents improving composites properties – e.g. Czarnecki and Chmielewska [11] used quartzite meal modified with silanes that positively influenced viscosity of the mix, adhesion between components and mechanical properties of vinyl ester composite.

Lately according to growing importance of sustainable development requirements including needs of utilizing wastes and saving raw substances the trend of applying wastes and by-products into polymer composites was observed. Bignozzi et al. [12,13] applied glass waste, rubber dusts of milled tires and cables into PC. Another trend is to use conventional fly ashes as the polymer composite microfillers – common additives in the cement technology. Using wastes or by-products in PC, except fulfilling sustainable development requirements, is important also from the economical point of view. High material cost of PC, resulting from the application of high quality components, is the main drawback against its wide use. However it can be reduced by replacing expensive components with cheaper equivalents, including waste products.

In the paper attention to fly ashes, the by-products of coal burning in energetics, used as the microfillers of concrete-like polymer composites was paid. The influence of fly ashes on composites properties may vary depending on the fly ash type, source and quality. Also important is whether properties of composites modified with fly ash are compared to properties of specimens containing alternative microfiller or containing no microfiller at all (just the coarse and fine aggregate of very low powder fractions content). In the literature more common is the second case – the analysis of the influence of additional very fine fractions or influence of partial substitution of fine aggregate with very fine fraction on selected composites properties.

The results of researches cited in the paper concern the application of the fly ashes, the by-products of coal burning in the conventional beds, into concrete-like polymer composites (including polymer mortars and concretes). Since fluidized calcium fly ashes, in comparison to conventional siliceous fly ashes, characterizes with different morphology (irregular shape of grains, much more developed surface specific area) and chemical composition (no glassy phase, no mullite, much higher calcium oxide content – including reactive CaO [14]) those results cannot be treated as a general information about the wide range of materials referred as fly ashes, including also the products of simultaneous coal burning and desulfurization of flue gases. Some conclusions concerning the conventional fly ashes were verified against the calcium fly ashes, yet the state of knowledge of concrete-like polymer composites with conventional ashes is a reference point for obtained results.

3. Effect of fly ash on concrete-like polymer composites

3.1. The influence of conventional fly ashes on fresh mix properties

The composition of polymer concrete/mortar mix can be characterized in different way. In this paper the composition of mixes presented in various papers analyzed here were often recalculated into parameters used in optimization approach, i.e.:

- A/B [g/g] – degree of filling the mix with aggregate, i.e. aggregate to binder ratio by mass.
- B/M [g/g] – microfiller to binder ratio by mass; Czarnecki [2] after analysis of the interdependence of micro-fraction of aggregate and resin binder as the appropriate indicates data from a range of 0.4 to 0.6).

The spherical shape of the conventional fly ash grains – in similar way as in cement concrete – may fill the empty voids between the larger grains of aggregate reducing intermolecular friction and facilitating mixing. It was confirmed by Gorninski [15] who tested polyester mortars (with ortho- and isophthalic polyesters) with addition of fly ash and showed that the presence of very fine fractions positively influenced workability of the mix. It is important to remember that the density of fly ash is usually lower than density of commonly used microfillers and substitution standard microfiller with fly ash results with higher volume of composite mix. Varughese and Chaturvedi [16] investigated influence of fly ash used as a substitute for river sand on polyester concrete mix parameters. It was found that in case of tested concretes with relatively high content of binder (A/B = 6.0 and A/B = 9.0) too high content of fly ash (more than 20% of total composite mass) decreased workability of the mixes. Varughese and Chaturvedi also showed that the higher fly ash content in the polyester concrete mass (despite the various degrees of filling A/B – Fig. 1a), the shorter curing time of PC mix was found.

The influence of fly ash on the viscosity of polymer composites mix was investigated e.g. by Soh et al. [6], who showed that the polyester micromortars containing the same, but not exceeding 40% of composite mass, amount of fly ash and calcium carbonate characterize with similar, almost constant values of viscosity, while higher content of microfiller caused increase of viscosity. Viscosity of the mix with fly ash was higher than viscosity of mix with calcium carbonate when the microfiller content was 40% (of composite total mass) – Fig. 1b. Authors explained that by lower density (2.16 g/cm^3) and larger surface specific area (Blaine: $3200 \text{ cm}^2/\text{g}$) of fly ash in comparison with CaCO_3 (density: 2.70 g/cm^3 , surface specific area: $2500 \text{ cm}^2/\text{g}$).

3.2. The influence of conventional fly ashes on the hardened composites properties

3.2.1. Mechanical strength

There is an opinion that addition of conventional fly ash, except technological parameters, improves also mechanical properties of polymer composites. Atzeni et al. [17] showed that partial replacing of fine aggregate with fly ash caused increase in compressive strength and flexural strength of epoxy mortars at shorter times of curing (at longer times strengths values were similar); Rebeiz et al. [18,19] estimated that 15% substitution of sand with fly ash in polymer concretes (including concretes reinforced with steel fibers) causes 30% increase in compressive strength of unreinforced concrete and 15% increase in flexural strength of fiber reinforced concrete. Other properties such as tensile strength, or shear strength did not show significant changes.

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