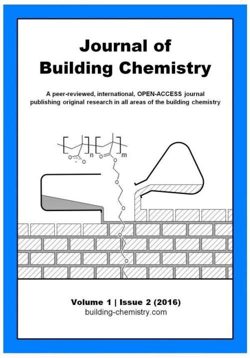


Available online at www.building-chemistry.com

Journal of Building Chemistry

J. Build. Chem. 1 (2016), 84-91

Technological properties of polymer concrete containing vinyl-ester resin waste mineral powder

Joanna Julia Sokołowska*

Department of Building Materials Engineering, Faculty of Civil Engineering, Warsaw University of Technology, Al. Armii Ludowej 16, 00-637 Warsaw, Poland

Abstract

The aim of the presented research was to assess the possibility of using waste mineral powder (remaining after preparation of aggregates for mineral-asphalt composites) as a component of polymer concrete with vinyl-ester resin used as the binder. The evaluation was done in terms of chosen technological properties, namely: consistence and temperature changes during setting of polymer mix. The first part of the paper contains material characteristics (chemical composition, particles size distribution, specific surface area) of mineral powders – both commonly used quartz powder and waste mineral powder – applied into polymer concrete as the finest fraction of aggregate. The second part of the research was focused on characteristics of setting of micro-mortars with vinyl-ester resin modified with the waste powder and consistence of concrete mixes prepared with use of those micro-mortars. Taking into consideration obtained data, author determined the optimal compositions of concrete with vinyl-ester resin and waste mineral powder of technical properties not worse than in case of regular (non-modified) one, but at the same time definitely more ecological.

Keywords: Polymer concrete; vinyl-ester resin; recycling; waste mineral powders; consistence testing

1. Introduction and research scope

Polymer Concretes (PC) are the cement-less building composites that consist mainly of two components: polymer binder (usually liquid synthetic resins such as epoxies, vinyl-esters, polyesters, etc.) and mineral aggregate. The aggregate used in polymer concretes includes fine and coarse natural or crushed stone materials. Very often these aggregates are of the same size, type and geological origin as in case of aggregates used in traditional cement concrete. However, since the polymer matrix in comparison to cement matrix characterizes with different values of physical properties such as hardness, brittleness or early shrinkage, the aggregate for PC often contains the very fine fraction called "microfiller" (Czarnecki et al. 1995). This fraction is prepared by grinding of rocks (e.g. quartz, granite, quartzite, limestone, etc.) or some waste materials – e.g. crushed ceramic or glass waste, rubber powder (Bignozzi et al. 2000, 2004) or industry by-products e.g. various fly ashes (Atzeni et al. 1990; Varughese and Chaturvedi 1996; Gorninski et al. 2007; Hraja et al. 2009; Czarnecki et al. 2010; Garbacz and Sokołowska 2010, 2013), perlite powder (Sokołowska et al. 2015, Jaworska et al. 2015), etc. Some of the wastes, because of their hydraulic properties, can be of course applied also in cement concrete

* Corresponding author. E-mail address: j.sokolowska@il.pw.edu.pl

Received: 19 December 2016 / Accepted: 23 December 2016 / Published: 30 December 2016
http://dx.doi.org/10.17461/j.buildchem.2016.203

(Jackiewicz-Rek and Woyciechowski 2011; Łukowski and Salih 2015; Jackiewicz-Rek et al. 2015), while some of them present chemical composition that excludes them as co-binders or active additives of type II. In such case the material is considered as the filler and is recommended to be applied in polymer concrete, rather than in cement concrete or polymer-cement concrete. Also for this reason, that the presence of very fine powders causes an increase in the value of water demand of the whole mix of cement concrete or polymer-cement concrete.

2. Materials and methods

In this study author attempted to use the waste mineral powder remaining after preparation of aggregates for mineral-asphalt composites as a component of polymer concrete. The waste powder was considered as the partial or total substitute of the quartz powder which is commonly used as the microfiller in PC technology. Both mineral powders were tested and compared, and later mixed with vinyl-ester resin binder and additional fine and coarse aggregates. For each micro-mortar (a mix of microfiller and polymer binder) the process of setting was analyzed. All mixes of concrete (prepared with use of those micro-mortars) were tested in terms of workability (test of consistence in two experimental ways). Taking into consideration obtained data, author determined the optimal compositions of concrete with vinyl-ester resin and waste mineral powder that characterized with technical properties not worse than in case of regular (non-modified) one but at the same time cheaper. The additional aspect of presented approach is finding a way of disposal of the waste material. Concrete containing waste powder instead of specially prepared quartz filler is definitely more ecological.

2.1. Components of tested vinyl-ester micro-mortars and concretes

Polymer binder. The resin used as the binder in the tested composites was the commercial vinyl-ester resin (VE). This vinyl-ester is a modified polyester resin, and the modification consisted in the introduction to the structure of the molecule fragments corresponding bisphenol epoxy resin. The chemical formula of such vinyl-ester is presented on Fig. 1. The modification was intended to obtain the resin of better mechanical properties (Table 1) with values similar to those of epoxy resins and high chemical resistance. Moreover, the products made from this resin retain the high strength characteristics in long-term contact with aggressive media. These properties make the resin suitable for the production of polymer concrete, laminates and other products, which are required high chemical resistance. For hardening the vinyl-ester resin a three-component curing system (Table 2) was used.

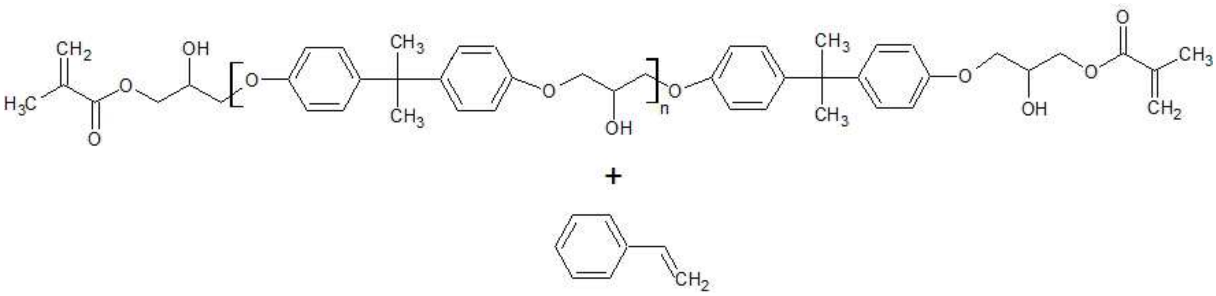


Fig. 1. Vinyl-ester resin (used as the binder in tested composites) before cross-linking.

Table 1. The properties of vinyl-ester resin used as the binder of tested mixes.

Property		Test method	Value
In the non-hardened state	Viscosity (25°C), mPa·s	DIN 53015	350 ± 50
	Gelling time (25°C), min	ISO 2535	30 ± 5
In the hardened state	Flexural strength, MPa	ISO 178	110
	Tensile strength, MPa	ISO 527	75
	Elasticity modulus, MPa	ISO 527	3500
	Extension, %	ISO 527	2.8
	Charpy impact strength, kJ/m^2	ISO 179	18
	Heat deflection temperature, °C	ISO 75	95
	Barcol hardness, °B	ASTM D 2583	35

Table 2. Three-component curing system for vinyl-ester resin used in tested mixes.

Component	Function	Content (according to resin mass), %
Cobalt naphthenate (concentration: 1%)	Accelerant	0.6
Dimethylaniline (concentration: 10%)	Accelerant	1.2
Methyl ethyl ketone peroxide (medium activity)	Hardener	2.0

Microfiller. The microfiller fraction consists of quartz powder and waste mineral powder. The commercially available quartz powder was prepared by grinding of pure quartz sand. The waste powder is a residue of the process of preparing aggregates for mineral-asphalt composites. Its chemical composition is therefore similar to the composition of original aggregates. On the Fig. 2 there are presented X-ray powder diffractogram and energy dispersive spectrum of waste powder. The XRD and EDS analysis showed that the main mineral component of the waste powder (about 85%) is calcite which is complemented by dolomite (D), quartz (Q) and trace amounts of clay minerals, namely illite (I) and kaolinite (K). The obtained data clearly showed the conformity of the tested powder with limestone, the basic rock the powder is derived from. More detailed characteristics of this kind of waste "limestone" powder one will find in paper by Kępniak et al. (2017).

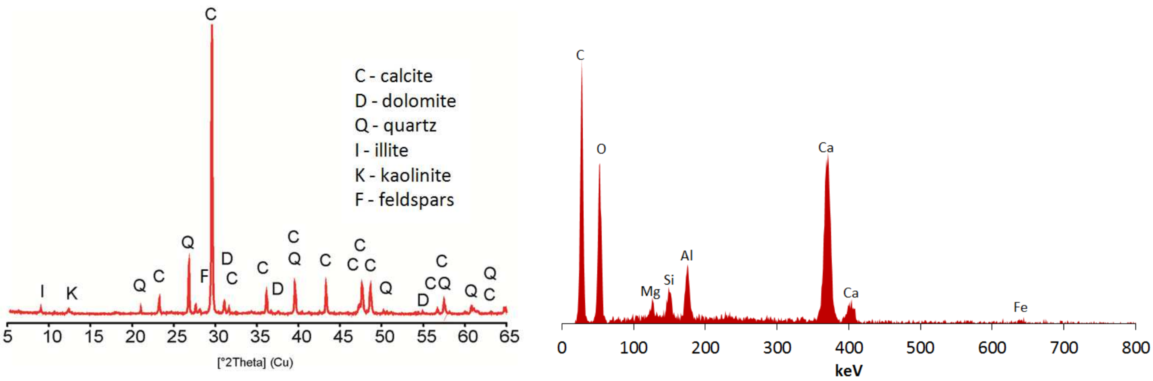


Fig. 2. Composition mineral powder: X-ray powder diffractogram (left), energy dispersive spectrum (right) – the detected components confirm the conformity with the aggregate the waste is derived from.

However, while the chemical composition of the waste remaining after preparation the particular type of aggregate in principle does not change, its granulometry does. Due to the variable parameters of the process of drying of aggregates during the year, the remaining powder grains size distribution changes. Powder collected in the winter is thicker, and in the summer – finer. The powder applied into polymer mix tested in the presented research was collected in winter. The grain size distribution of the waste powder as well as the quartz powder determined in the laser analyzer is showed on the Fig. 3.

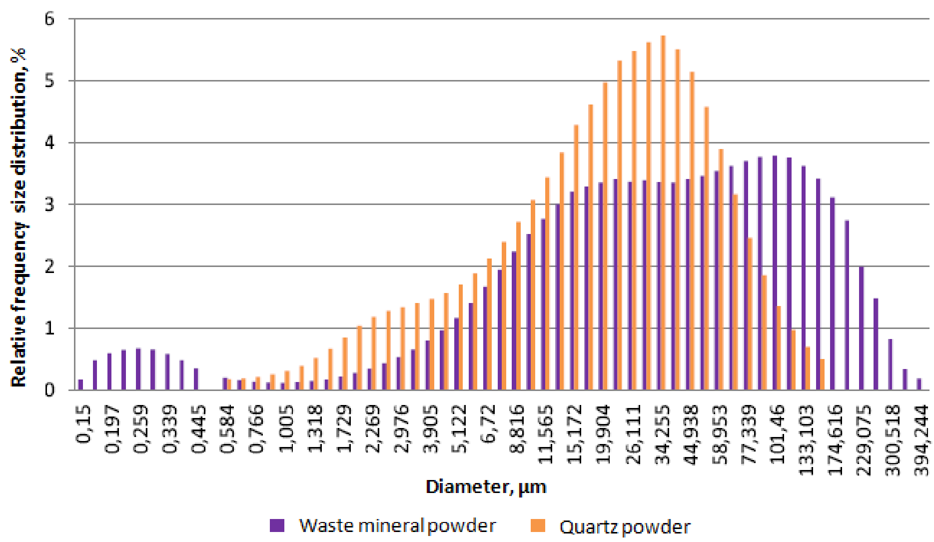


Fig. 3. Relative frequency of grain size distribution of waste powder and quartz powder.

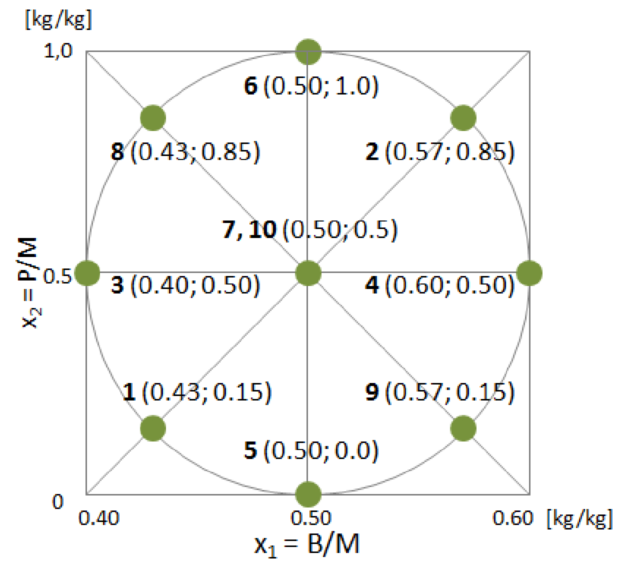
The tested powders differ in granulation. Waste mineral powder consists of grains of size 0.15 ÷ 394.24 µm, while quartz powder consists of grains of size 0.58 µm ÷ 152.45 µm. The size distribution of quartz powder is described by only one mode (31.96 µm) while the size distribution of waste powder is bimodal (0.26 µm and 94.84 µm). In general the waste powder consists of more bigger grains (average grain size: 60 µm, D_{50} = 39.23 µm, D_{90} = 174.62 µm) than quartz powder (average grain size 28.03 µm, D_{50} = 22.80 µm, D_{90} = 67.52 µm) but at the same time it contains particles smaller than 0.58 µm. As a result, the specific surface area of tested waste mineral powder (14 585 cm^2/cm^3) is over twice as large as in case of quartz powder (6 950 cm^2/cm^3). This may affect the consistence of the polymer micro-mortar and concrete polymer mix containing such waste material.

Fine and coarse aggregates. The additional aggregate used to prepare tested concrete mixes included standard sand (in conformity with EN 196-1) and natural gravel of fraction 4-8 mm in a ratio of 1:2 (by mass). The coarse aggregate was washed and dried to remove additional dust and ensure precise dosing of microfiller to the mix.

2.2. Research statistical design

As the criteria of evaluation of the influence of mineral waste powder on mix quality the following properties were selected: temperature and time during setting of micro-mortars and workability of concrete mix expressed by consistence. The experiment was prepared according to statistical design of two variables and 9 experimental points (with twice hold repetition of central point of experiment – compare points 7, 10) presented in Table 3. Statistical designs were earlier discussed and successfully used by author for designing various polymer composites (Czarnecki and Sokołowska 2011, 2015; Garbacz and Sokołowska 2013), enabling elaboration of mathematical models very well suited to the experimental data. In the design the chosen input variables were: x_1 = B/M, x_2 = P/M (relative ratios by mass where: B – binder, M – microfiller including quartz powder and waste mineral powder, P – waste mineral powder). The first variable range was 0.40 ÷ 0.60. The second variable range was 0.0 ÷ 1.0. The substitution of quartz powder was proceeded by mass. It was possible because the density of quartz powder (2.650 kg/dm3) and waste powder (2.621 kg/dm^3) were not significantly different.

Table 3. The compositions of tested mixes of polymer concrete with various contents of vinyl-ester resin and microfiller (including quartz powder and waste mineral powder in various proportions).

Statistical design	No in design	Component per 1 m^3 of concrete [kg]				
		Resin	Quartz powder	Waste powder	Agg. 0-2 mm	Agg. 4-8 mm
	1	138	275	47	667	1333
	2	158	40	236		
	3	133	166	166		
	4	161	134	134		
	5	148	296	0		
	6	148	0	296		
	7	148	148	148		
	8	138	47	275		
	9	158	236	40		
	10	148	148	148		

2.3. Test methods

2.3.1. Temperature and time during setting

Testing of time and temperature during setting of the micro- mortars was carried out starting from mixing the resin and the curing agents set with the microfiller until occurrence of maximum temperature of the system. Such time is considered as the "hardening time" and the maximal temperature is considered as "setting temperature". In addition, based on the charts describing time-temperature relation. workability time and gelation time were determined.

2.3.2. Consistence of concrete mix – cone penetration procedure

The study was conducted according to the method described in PN-85/B-04500. The test result was the value of penetration depth of cone weighing 300 g into the tested mix located in the cone-shaped container. The study was performed in each case 10 minutes after mixing the components of concrete.

2.3.3. Consistence of concrete mix – flow table procedure

The study was conducted according to the modified procedure described in EN 1015-3: the sample of mix was placed on the flow table and shaken 30 times within 30 seconds. The test result was the average of two (perpendicular) diameters of the flowed mix. The study was performed in each case twice: 10 minutes and 30 minutes (estimated gelation time) after mixing the components of concrete.

3. Results and discussion

3.1. Temperature and time during setting

The influence of waste mineral powder on setting process was evaluated by measuring the temperature in time of setting the micro-mortars containing vinyl-ester resin and various contents of quartz powder and waste powder. It was confirmed that the more microfiller was in the micro-mortar (the lower B/M ratio), the longer were workability time, gelation time and the time of occurrence of the maximal temperature (which also obtained the lower value). On the Fig. 4 (left) there is presented the temperature in time of setting registered for chosen micro-mortars containing various contents of resin and microfiller (each time the microfiller consisted of 50% of quartz powder and 50% of waste powder, P/M = 0.5) that clearly illustrates abovementioned observation.

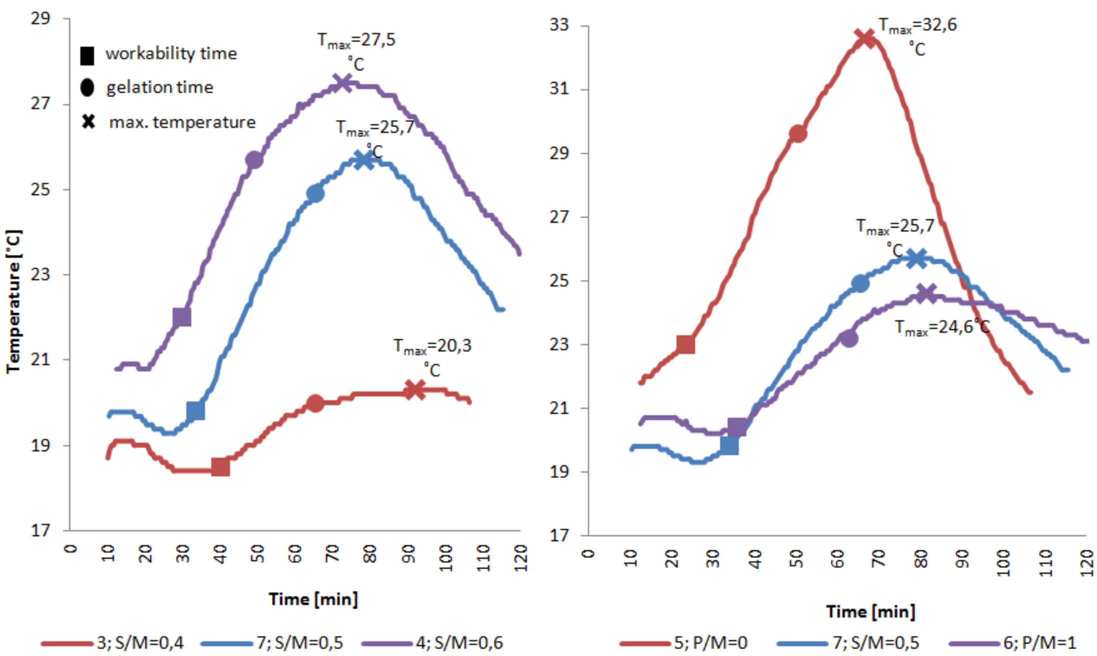


Fig. 4. Temperature in time of setting of vinyl-ester micro-mortars of various content of polymer but the same proportion of quartz and waste powders in microfiller: P/M = 0.5 (left) and different proportions of powders but constant polymer to microfiller ratio B/M = 0.5 (right).

Moreover it was showed that the presence of waste mineral powder in the microfiller fraction also caused the extension of workability time, gelation time, time of occurrence of the maximal temperature and lowering the value of maximal temperature. The higher was the content of waste powder in the total microfiller, the longer were the times and lower was the temperature. However analysis of the results showed that when substitution of quartz powder with waste mineral powder was done on the level of 50% and more, the effect on analyzed parameters was similar. This finding is showed on Fig. 3 (right) presenting temperature in time of setting registered for micro-mortars of S/M = 0.5 containing 0%, 50% and 100% of waste powder in total microfiller fraction (i.e. P/M = 0.0, 0.5, 1.0) – last two cases are considered to be very similar.

In general extension of the gelation time of the hardened system may be considered as the positive effect from the technical point of view as there is more time for mixing and molding the elements or cleaning the equipment and tools used to produce the polymer mix. However lowering the temperature of the system too much may mean that the polymerization does not occur fully. Therefore, before performing tests of the mechanical strength of hardened composites, it is safer to choose compositions, where the effect of the presence of waste powder on the temperature is not so strong.

3.2. Consistence of concrete mix

Examination of the consistence of polymer concrete mixture was performed for the mixes that were created by mixing previously investigated micro-mortars with fine aggregate (sand) and coarse aggregate (gravel). Thus, the analyzed variables – binder to microfiller ratio (B/M) and waste powder to microfiller ratio (P/M) remain the same.

Although the testing was done in two ways, using two methods (cone penetration procedure, flow table procedure), in both the cases it was showed that the more microfiller or less resin binder were introduced into the mix (i.e. B/M value was lower), the blend presented lower fluidity. However, this is an expected conclusion. More interesting was to determine effect of the presence of waste mineral powder, thus the effect of the second variable, on the consistence. Both studies showed that the more waste powder was in microfiller (i.e. the higher was P/M), the concrete mix was less fluid. In case of the cone penetration method it was shown that the depth of cone penetration decreased linearly with the content of the waste powder (at 100% substitution of quartz powder with waste, the penetration depth changed from 28.5 mm to 14.0 mm) – Fig. 5.

In case of flow table method the tendency was similar, although the effect was not so spectacular – neither in the case of the test carried out after 10 minutes – Fig. 6 nor after 30 minutes – Fig. 7. However, it was found that at higher resin content (B/M >= 0.55) and waste mineral powder in amount of 40 ÷ 50% of total microfiller, consistence of concrete was only slightly worse. This is highly advantageous from the ecological point of view (reuse of large share of waste), though one need to remember that the higher content of the resin results in a higher cost of the whole composite.

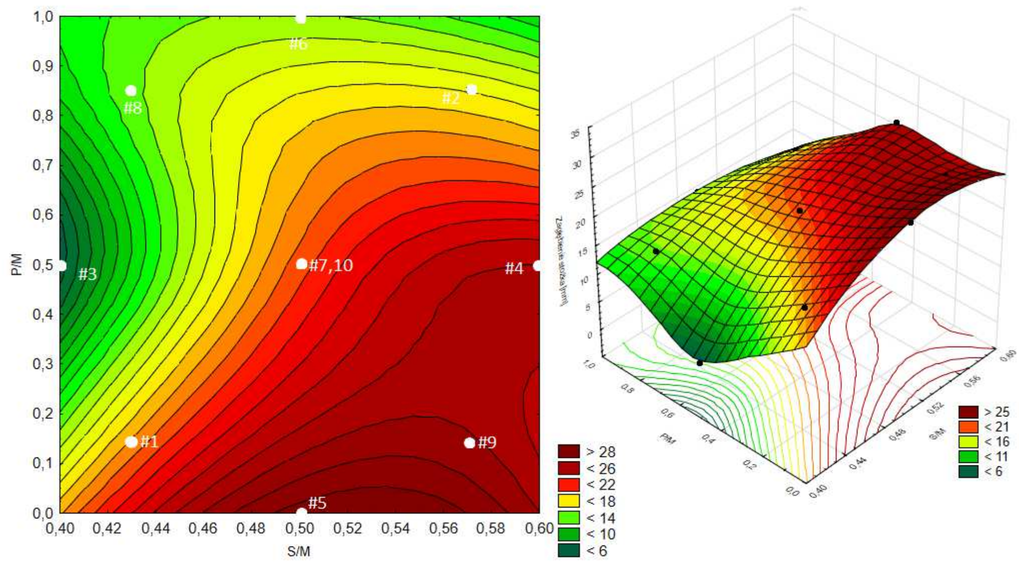


Fig. 5. Consistence of polymer concrete mix tested according to cone penetration procedure (10 minutes after mixing) vs. the material variables x_1 = B/M (polymer binder to microfiller mass ratio), x_2 = P/M (waste powder to microfiller mass ratio).

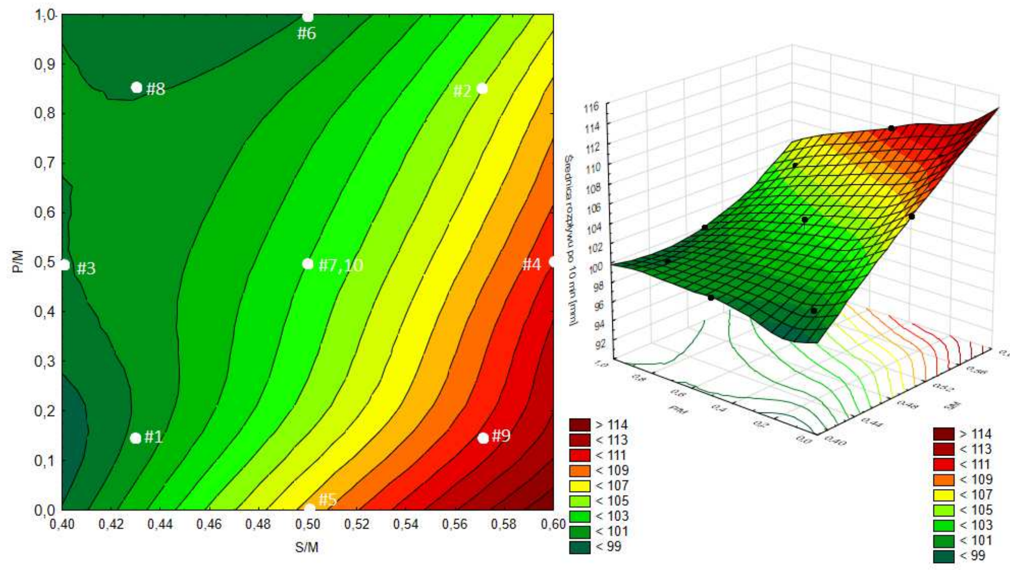


Fig. 6. Consistence of polymer concrete mix tested according to flow table procedure (10 minutes after mixing) vs. the material variables x_1 = B/M (polymer binder to microfiller mass ratio), x_2 = P/M (waste powder to microfiller mass ratio).

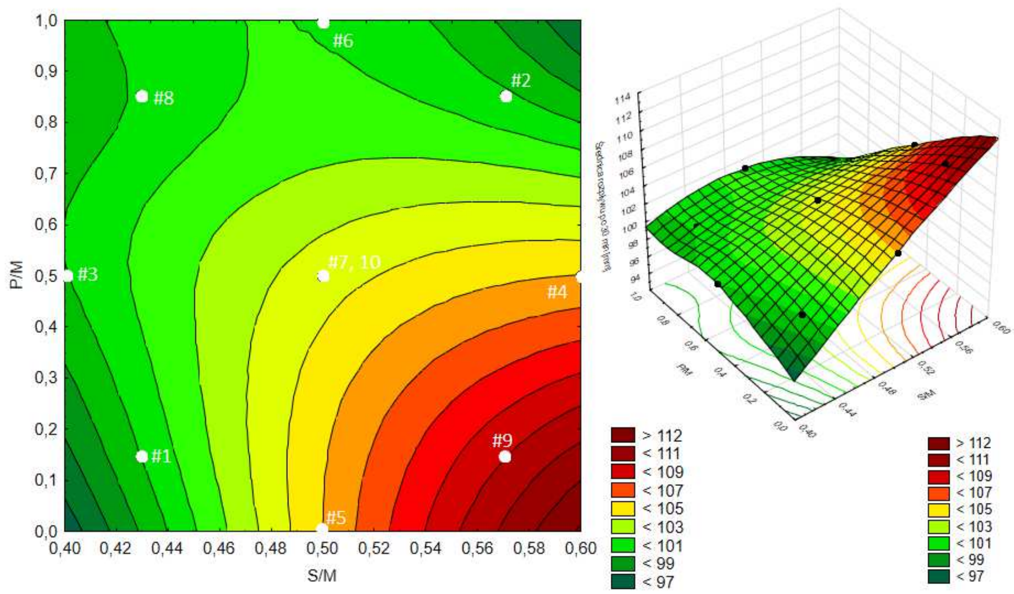


Fig. 7. Consistence of polymer concrete mix tested according to flow table procedure (30 minutes after mixing) vs. the material variables x_1 = B/M (polymer binder to microfiller mass ratio), x_2 = P/M (waste powder to microfiller mass ratio).

4. Conclusions

The analysis of presented results showed that using collected in winter waste mineral powder remaining after preparation of aggregate (of limestone) for mineral-asphalt composites in polymer concretes with vinyl-ester resin is possible, but the composites should be carefully designed in terms of consistence. Although the density of the waste material is not very different than the density of commonly used quartz microfiller, the granulation of the waste is different and is resulting in much more developed specific surface area. This creates the need to add more polymer binder to cover properly each waste powder grain and to provide good workability of mix of composite containing such waste. This finding was confirmed by the measurements of temperature of micro-mortars during their setting: the more waste material was in the micro-mortar, the longer were the subsequent steps of setting and the lower was temperature of micro-mortar. In some range this could be treated as a positive effect as longer gelation time means more time for preparation and molding the polymer concrete element.

The results of consistence tests done with two methods showed the impact of presence of waste mineral powder on the consistence of concrete mix: the more waste powder in the mix, the less fluid consistence and more dense mix. Taking into account the obtained results and cost of materials, as the economic-technical-ecological compromise, the optimal compositions in the area of presented experiment may be indicated those close to the point of the experiment described by variables B/M = 0.571 and P/M = 0.146. In other words, it is reasonable to use concrete compositions with vinyl-ester resin, wherein the binder/microfiller relative ratio is at least 55%, as in such case quartz powder may be replaced by waste powder in the large share. However this optimization should be confirmed in study on mechanical strength of composites.

Author take into consideration designing polymer concrete that contains waste materials applied into mix not only as the microfiller but also as fine and coarse aggregate (author has already tested polymer concrete with quartz powder, sand and high density polypropylene waste as the gravel substitute – see Sokołowska et al. 2013) or as additional fibers. Wiliński et al. (2016) introduced recycled PET fibers into cement concrete, however applying them into polymer concrete would provide better compatibility, since the adhesion between PET and polymer binder is better than between PET and cement binder.

Acknowledgements

Author is thankful to Katarzyna Osowska for help in performing the research study. The paper was prepared in the framework of Warsaw University of Technology Grant.

References

Atzeni C., Massidda L., Sanna U.: Mechanical properties of epoxy mortars with fly ash as filler. Cement and Concrete Composites 12 (1990), 3-8.

Bignozzi M.C., Saccani A., Sandrolini F.: New polymer mortars containing polymeric wastes. Part 1. Microstructure and mechanical properties. Composites Part A: Applied Science and Manufacturing 31 (2000), 97-106. http://dx.doi.org/10.1016/S1359-835X(99)00063-9

Bignozzi M.C., Saccani A., Sandrolini F.: Glass waste valorization in advanced composite materials. In: "Proc. 11th int congress on polymers in concrete – ICPIC '04" Maultzsch M editors. Berlin; 2004. 587-595.

Czarnecki L., Garbacz A., Kurzydłowski K.: Morphology of polymer concrete microstructure. In "Proc. 8th int congress on polymers in concrete – ICPIC'95" Van Gemert D editor. Oostende, 1995. 299-304.

Czarnecki L., Garbacz A., Sokołowska J.J.: Fly Ash Polymer Concretes. In: "Proceeding of the second international conference on sustainable construction materials and technologies–SCMT", Ancona, 2010. 127-137.

Czarnecki L., Sokołowska J.J.: Optimization of polymer-cement coating composition using material model. Key Engineering Materials 466 (2011), 191-199. https://dx.doi.org/10.4028/www.scientific.net/KEM.466.191

Czarnecki L., Sokołowska J.J.: Material model and revealing the truth. Bulletin Of The Polish Academy Of Sciences Technical Sciences, 63 (2015), 7-14. http://dx.doi.org/10.1515/bpasts-2015-0001

EN 196-1, 2016. Methods of testing cement. Determination of strength. European Standard.

EN 1015-3, 2000. Methods of test for mortar for masonry. Determination of consistence of fresh mortar (by flow table). European Standard.

Garbacz A., Sokołowska J.: Effect of calcium fly ash on PC properties. In: Proceeding of the 13th international congress on polymers in concrete – ICPIC 2010, Funchal-Madeira; 2010. 281-288.

Garbacz A., Sokołowska J.J.: Concrete-like polymer composites with fly ashes – comparative study. Construction and Building Materials 38 (2013), 689-699. http://dx.doi.org/10.1016/j.conbuildmat.2012.08.052

Gorninski J.P., Dal Molin D.C., Kazmierczak C.S.: Strength degradation of polymer concrete in acidic environments. Cement and Concrete Composites 29 (2007), 637-645. http://dx.doi.org/10.1016/j.cemconcomp.2007.04.001

Harja M., Bărbuță M., Rusu L.: Obtaining and characterization of the polymer concrete with fly ash. Journal of Applied Sciences 9 (2009), 88-96. http://dx.doi.org/10.3923/jas.2009.88.96

Jackiewicz-Rek W., Woyciechowski P.: Carbonation rate of air-entrained fly ash concretes. Cement Wapno Beton 5 (2011), 249-256.

Jackiewicz-Rek W., Załęgowski K., Garbacz A.: Properties of cement mortars modified with ceramic waste fillers. Procedia Engineering 108 (2015), 681-687. http://dx.doi.org/10.1016/j.proeng.2015.06.199

Jaworska B., Sokołowska J.J., Łukowski P., Jaworski J.: Waste mineral powders as a components of polymer-cement composites. Archives of Civil Engineering 61 (2015), 199-210. https://doi.org/10.1515/ace-2015-0045

Kępniak M., Woyciechowski P., Franus W.: Chemical and physical properties of the waste limestone powder as a potencial microfiller of polymer composites. Archives of Civil Engineering (2017); acceped for publication.

Łukowski P., Salih A.: Durability of mortars containing ground granulated blast-furnace slag in acid and sulphate environment. Procedia Engineering 108 (2015), 47-54. https://dx.doi.org/doi:10.1016/j.proeng.2015.06.118

PN-85/B-04500. Bulding mortars. Examination of physical and strength properties (in Polish). Polish Standard.

Sokołowska J.J., Piotrowski T., Garbacz A., Kowalik P.: Effect of introducing recycled polymer aggregate on the properties of C-PC composites. Advanced Materials Research 687 (2013), 520-526. https://dx.doi.org/10.4028/www.scientific.net/AMR.687.520

Sokolowska J.J., Woyciechowski P.P., Łukowski P., Kida K.: Effect of perlite waste powder on chcemical resistance of polymer concrete composites. Advanced Materials Research 1129 (2015), 516-522. https://dx.doi.org/10.4028/www.scientific.net/AMR.1129.516

Varughese K.T., Chaturvedi B.K.: Fly ash as fine aggregate in polyester based polymer concrete. Cement and Concrete Composites 18 (1996), 105-108. http://dx.doi.org/10.1016/0958-9465(95)00006-2

Wiliński D., Łukowki P., Rokicki G.: Application of fibres from recycled PET bottles for concrete reinforcements, Journal of Building Chemistry 1 (2016), 1-9. http://dx.doi.org/10.17461/j.buildchem.2016.101