The use of rubber granules from tire recycling as geopolymers filler.

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Abstract

Waste management is currently one of the most important issues. One of the main sources of rubber waste are worn car tires. This problem have led to the increasing research focus on the useful application of rubber granules derived from the recycling of tires. The paper presents an overview of the literature about concrete and geopolymer with addition of rubber granules and their physical, mechanical and acoustic properties. Moreover, the article contains the results of research on geopolymer based on fly ash with rubber granules partially replacing sand. Control samples with a sand content of 25% and 50% and also samples containing sand and rubber granulate in equal proportion of 12.5% or 25%, were investigated. The rubber granules derived from the recycling of car tires in two sizes of particles: 0.0 - 0.8 mm and 1 - 4 mm, were used. The results of testing density, compressive strength and abrasibility were presented. A positive effect of the addition of rubber granules on abrasion resistance was observed.

Keywords: geopolymer; rubber granules

1. Introduction

Nowadays, the motorization industry is developing very dynamically. This causes a large amount of rubber waste. They are not only tires but also washers, gaskets, suspension elements, tubes - hoses. Within one year globally 1 billion Mg car tires are withdrawn from exploitation. In Poland, the annual production of car tires is set up around 180,000 Mg. As the tire weight is reduced by 20 - 25% during utilisation, about 140,000 Mg used tires remain to management. In addition, there is about 10,000 Mg other rubber waste from dismantling cars left to be reorganized [1].

A very large amount of rubber waste, including used tires, poses a serious threat to the environment, since they do not dissolve in organic solvents or are not biodegradable. Features of tires useful while exploitation cause problems after withdrawn them from use. Huge landfills of used tires carry another threat to the environment, which is the possibility of their self-ignition. Burning a large number of tires in the open air causes air pollution with toxic smoke, soil degradation, groundwater contamination, destruction of flora and fauna [2, 3].

These and other environmental aspects have resulted in the legal regulations concerning the management of worn tires and rubber. These regulations prohibit the storage of waste tires in landfills (in the EU Directive 1999/31/EC and the Polish Act from 27 April 2001), introduce the obligation to obtain an appropriate level of recovery and recycling of tires for manufacturers and importers (the Polish Act from 11 May 2001) and the obligation to dismantle and reuse tires before the vehicle is scrapped (in the EU Directive 2000/53/EC, the Polish Act from January 20 2005) [4].

There are many methods for the management of used tires. One of them is product recovery, which includes cutting the tread, remolding and the use of worn tires for purposes other than their original. Another method is energy recovery in which worn tires are used as an alternative fuel to recover energy in the form of heat. Tires are combust in whole or after comminution as a base fuel or as an addition to another type of fuel. Tires are characterized by a relatively high calorific value in comparison to other fuels generally used. Recycling of used tires and other rubber waste can be carried out by thermolysis and pyrolysis, resulting in a gas, liquid and solid fraction. However, rubber material recycling can be carried out by its regeneration, i.e. devulcanization, which consists in the breaking of bonds that build the network: carbon - sulfur, sulfur - sulfur and the partial destruction of elastomer chains. The resulting regenerate, depending on the degree of its degradation, can be further processed and vulcanized to obtain a new product. Physical, mechanical, thermal and chemical methods of devulcanization are used. Mechanical recycling of used tires and rubber waste consists in their fragmentation and subsequent re-use [1, 3, 4]. The subject of the conducted research was the possibility of using rubber granules derived from the recycling of used tires as a filler in geopolymers.

1.1. Conventional and geopolymer concretes with addition of rubber granules

One of the Universities that have carried out studies of conventional concrete with rubber granules was the Wroclaw University of Technology. Four series of samples I-IV were prepared containing, respectively: 0, 100, 200 and 300 kg of rubber granules, per 1 m³ of concrete mix. Rubber granules with a particle size of 2.5-4 mm was used. Compressive strength, tensile strength and modulus tests were performed after 28 days of sample aging. It was observed that after increasing the amount of rubber granules, density and mechanical properties of
concrete decrease. The value of compressive strength decreased by about half, the value of tensile strength decreased about 1.5 times, and the value of modulus of longitudinal elasticity more than 1.5 times for each subsequent series [5].

The impact of the addition of rubber granules on the properties of concrete was also examined at the Bialystok University of Technology. To make the concrete mix, a rubber granules with a particle size of 0 - 2 mm, a gravel mixture of 2 - 8 mm, river sand rinsed 0 - 2 mm and Portland CEM I 32.5 cement was used. Samples were prepared: without and with rubber granules, which were used to partly replace natural aggregate in the amount of 10%, 20% and 30% by volume, so final samples contained 2%, 4% and 6% of the rubber granules, respectively. The tests of compressive strength were carried out after 28, 90 and 180 days. For samples with 2%, 4% and 6% of the rubber granules, compressive strength decreased compared to samples without granules, by about 20%, 25% and 33% respectively, irrespective of the aging period of the samples. As the amount of rubber granules increased, the density of concretes decreased, as well as their absorbability, by about 13%, 20% and 29% respectively for samples with 2%, 4% and 6% of the rubber granules, compared to the control samples [6].

The study of geopolymer concrete with the addition of rubber granules was carried out at the University of Texas at Arlington. The influence of changing factors on compressive strength was investigated. The variable factors were: the amount of rubber granules added, which partly replaced fine aggregate: 5, 10, 15 or 20% (by volume), the size of coarse aggregate particles: 9.5 or 16 mm and the ratio of sodium silicate (Na$_2$SiO$_3$) to sodium hydroxide (NaOH): 0.5 or 2.0. The base for geopolymer concrete was fly ash class C (containing 8-20% CaO). The rubber granules with size of 1 - 2 mm and alkaline liquid (as mixture of sodium silicate solution Na$_2$SiO$_3$ and 14 molar sodium hydroxide solution NaOH), were used. The samples were made in cylindrical shape and with dimension 100x200 mm, cured at a temperature of 30°C and a relative humidity of 70%. Then, after 7 days from their production, they were subjected to a compressive strength test in accordance with ASTM C39 (American Standard Testing and Material). It was observed the addition of rubber granules had a negative effect on compressive strength. However, a significant effect on the compressive strength was observed when replacing 20% (by volume) of the fine aggregates with rubber granules. Higher compressive strength was also observed using a larger fraction of a rubber granules and at a higher ratio of sodium silicate (Na$_2$SiO$_3$) to sodium hydroxide (NaOH) [7].

In other studies on geopolymer with the addition of rubber, the following properties were tested: impact strength, compressive strength, porosity and heavy metal leaching. For the production of samples was used rubber dust, with a particle size below 0.9 mm, clay with 45% kaolinite (activated at 750°C for 6 hours) and quartz sand with a particle size below 0.5 mm. Prepared mixtures were poured into molds and allowed to cure for 3 days. Then, after removing from the molds, the samples were left in the laboratory conditions to dry for 15 days. Samples were produced with a rubber dust content ranging from 0 to 30% and also samples containing both sand and rubber dust. For the leachability test deionized water and 0.1 molar HCl solution, were used. The content of zinc in acid leachates was detected. It was observed that while increasing the content of rubber dust, content of zinc increases as well. For samples with up to 25% fine rubber, the zinc content did not exceed the limit values (5 mg/L). Analyzing the results of the porosity test, it was found that the porosity of materials decreases when the percentage of rubber dust or sand increase. The value of compressive strength decreased when the content of rubber dust increase, however it was not related to the sand content. The impact strength subtly decreased with an increase in the content of rubber dust to 5%, and then remained at a similar level [8].

### 1.2. The influence of the addition of rubber granules on the acoustic properties of conventional and geopolymer concrete

The aim of the research conducted by Ghizdavet was to determine the possibility of using concrete with the addition of rubber granules as sound absorbing material. CEM II / AV 42.5R cement, fine aggregate with particle size of 0.063 - 2 mm, coarse aggregate with a particle size of 2 - 16 mm, rubber granules (styrene - butadiene rubber) which is waste from sports fields with particle size of 0.5 – 4 mm were used to produce a concrete mix. Rubber granules were replaced with small aggregate in the amount of 0%, 5% and 7.5% (by weight). A polycarboxylate ether was used as a superplasticizer. Since the rubber particles are characterized by a smooth surface, which makes it difficult for the cement to bind them, the rubber granules are immersed in a 1 molar solution of sodium hydroxide before being added to the concrete mix. The purpose of this treatment was also to increase the hydrophilicity of the surface of the rubber particles. Then the rubber granules was washed not to change the chemical composition of the concrete mix and next dried. Three series of samples were prepared, with different ratio of water to cement: 0.45, 0.50, 0.55. For the material composition, which was characterized by the best sound absorption coefficient (material composition with a water-cement ratio of 0.50 and the addition of 7.5% rubber granules), four additional samples were created in which macroscopic pores were shaped. For the first three samples, a cylindrical, rectangular, square pore shape was made accordingly. The fourth sample contained all kinds of pore shapes. The depth of the resulting pores ranged from 10 - 17.6 mm. The sound absorption coefficient was tested using an acoustic interferometer in the frequency range 200 - 3000 Hz. The sound absorption coefficient of samples not containing rubber granules, depending on the ratio of water to cement, was in the range of 0.22 - 0.37. Assuming a sound absorption coefficient of 0.5, as the boundary above, the material being classified as sound-absorbing, it can be concluded that all material compositions containing rubber granules met this condition. The highest values of the sound ab-
The sound absorption coefficient were obtained for samples with a water to cement ratio of 0.5 and a rubber granules content of 5% and 7.5%, respectively 0.93 and 0.82. Higher values of the sound absorption coefficient were expected for a sample containing 7.5% rubber granules. However, the sample containing 5% rubber granules was accidentally mechanically damaged while preparation phase, so it was considered together with the preferred arrangement of the rubber particles as a reason for obtaining a high absorption coefficient. For this reason, additional samples were made with macroscopic pores, which increase the surface of contact with the sound. Sound absorption coefficient values of these samples were in the range of 0.6 - 0.7, and the highest values were in the frequency range 1000 - 1200 Hz, except for the sample with macroscopic pores in the shape of rectangles, which the highest value of the sound absorption coefficient was in lower frequencies [9].

The research conducted by Mahommad concerned hollow concrete blocks in which a part of the fine aggregate was replaced with a rubber granules. To produce the samples, Portland cement type I, fly ash class F, silica fume, coarse aggregate (gravel), fine aggregate (river sand) and rubber granules were used. Silica fume was used to improve the bond between the concrete mix and the rubber granules. In total, sixty-four material compositions were produced, differing in content: fly ash (5%, 15% and 30% by volume relative to the cement content), silica fume (5%, 10% and 20% by volume relative to the cement content), rubber granules (replacing fine aggregate at 0%, 10%, 25% and 50%). All material compositions were subjected to a compressive strength test after 28 days of aging. After analyzing the results, three series of material compositions were selected, which were subjected to further testing. Each batch of material composition contained 15% fly ash, the series varied in the content of silica fume, which was 0%, 5% and 10%. Samples containing 0%, 10%, 20% and 50% rubber granules were prepared in each series. The sound absorbing test was carried out in accordance with ASTM E1050, using an impedance tube method. The sound transmission loss was carried out on the same apparatus using a set of transmission sound loss tube, a sample holder and an additional extended pipe. The sound transmission class was calculated in accordance with the requirements of ASTM E413. The value of the sound absorption coefficient and the noise reduction coefficient increased with increasing content of the rubber granules. According to the authors of the study, this is due to the sound absorption by the air trapped on the surface of the rubber particles. On the other hand, the increase of the silica fume content for the same contents of the rubber granules caused a decrease in the value of these coefficients. It was observed that this is due to the fact that silica fume acts as a micro filler. The transmission loss coefficient decrease along with the increase in the content of rubber granules. Regardless of the content of rubber granules, the tested material compositions are in the same sound transmission class, however the sound transmission value expressed in decibels decreases by about 2.5 dB with the increase content of the rubber granules from 0% to 50% [10].

Holmes' research has focused on the effect of the addition of rubber granules with different fractions on the acoustic properties of concrete panels. CEM I cement, fine and coarse aggregate as well as rubber granules were used to make the samples, which replaced the fine aggregate in 7.5% and 15%. Rubber granules with fractions: dust, 1 - 3 mm, 2 - 6 mm, 10 - 19 mm were used. The water to cement ratio was 0.47. Nine panels with dimensions of 245x245x100 mm were produced for each material composition. In order to determine the sound absorption coefficient, tests were conducted in which reverberation times were recorded in the room, both when there was no sample in it and when its surface was partially lined with prepared samples. The sound absorption coefficient was calculated based on the reverberation time (average of ten tests), the measured room volume and the area with the samples. The sound insulation of materials was determined on the basis of the sound intensity (dB) measured through concrete panels placed in the duct between two rooms, using low (63, 125, 250, 500 Hz) and high (1000, 2000, 4000, 5000 Hz) frequencies sound. These tests were also carried out on samples that were previously heated in an oven at 75°C for 24 hours and for samples previously kept at -15°C for 24 hours. The sound absorption coefficient for samples containing rubber granules is 0.013 - 0.2, while for control samples not containing rubber granules, it is 0.018. The value of the sound absorption coefficient increased with the increase of the content of rubber granules and with the increase of the rubber granules fraction. The increase in the replacement of fine aggregate by rubber granules from 7.5% to 15% resulted in an increase in the sound absorption coefficient by 623%, 107%, 33%, 21% for dust, fraction 1 - 3 mm, fraction 2 - 6 mm, fractions 10 - 19 mm, respectively. The sound absorption coefficient for samples that were subjected to heating or freezing did not significantly change its value. It was found that concrete with the addition of rubber granules is more effective in absorbing the sound from ordinary concrete both at room temperature and at lower or higher temperatures. The results of the acoustic insulation test at low frequencies show similar results for conventional concrete as well as with rubber granules at 63 and 125 Hz, while at 250 and 500 Hz frequencies conventional concrete exhibits slightly more insulation (by 4 - 5 dB) than concrete with rubber granules. In the high frequency range (1,000, 2,000, 4,000 and 5,000 Hz), conventional concrete exhibits better sound insulation, with an average improvement of 5 dB. Corresponding results were found for samples subjected earlier to lower and higher temperatures. Since concrete with rubber granules is characterized by better sound absorption, it has been concluded that it can be effectively used as a sound absorbing material [11].

Research on geopolymer with rubber granules consisted in determining its acoustic insulation property. Metakaolin, fine aggregate (sand), coarse aggregate (gravel, grain size 4.75 - 12.5 mm) and rubber granules with particle size below 1 mm were used to make the mixture. Samples were prepared and 0%, 2%, 6%, 10% and 14% (by weight) of natural aggregates were replaced by the rubber granules. The samples were hardened at 65°C.
for 48 hours. The tests were also carried out on samples made of conventional concrete for comparison purposes. The geopolymer concrete samples with rubber granules showed better properties. The highest values of the sound absorption coefficient and the noise reduction coefficient were found in samples with 10 and 14% replacement of the aggregate with rubber granules. The highest sound transmission loss had samples in which the aggregate was replaced with rubber granules in the amount of 0, 2 and 6% [12].

2. Materials and methods

2.1. Materials

The rubber granules used in this research were manufactured by the Zakład Produkcji Granulatu Gumowego ORZEL S.A. For the preparation of samples rubber granules with fractions: 0.0 - 0.8 mm, shown in Fig. 1 and 1 - 4 mm, shown in Fig. 2, were used [13].

![Figure 1. Rubber granules 0.0 – 0.8 mm [13].](image)

![Figure 2. Rubber granules 1 – 4 mm [13].](image)

Geopolymers were made based on fly ash from bituminous coal combustion in the grate boilers from the Skawina power plant. The chemical composition of fly ash is shown in Table 1, and the physical properties in Table 2 [13].

<table>
<thead>
<tr>
<th>Table 1. The chemical composition of fly ash [13].</th>
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<tr>
<td>Parameter</td>
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<tr>
<td>Loss of ignition [%mass]</td>
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<tr>
<td>SiO₂</td>
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<tr>
<td>Al₂O₃</td>
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<tr>
<td>Fe₂O₃</td>
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<tr>
<td>CaO</td>
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<td>MgO</td>
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<th>Table 2. Physical properties of fly ash [13].</th>
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<tr>
<td>Parameter</td>
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<tr>
<td>Fineness [% mass]</td>
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<td>Density [kg/m³]</td>
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</table>
| Indicator of pozzolanic activity [%]:
  | |
  | After 28 days | 92.0 |
  | After 90 days | 108.8 |

2.2. Preparation of samples

For the preparation of the alkaline solution, technical sodium hydroxide in the form of flakes and aqueous solution of sodium silicate R - 145 with a density of 1.45 g/cm³ and a mole module of 2.5, were used. The solution was prepared with tap water and let to equalize the temperature and the concentrations of ingredients [13].

Depending on the composition being prepared, specific amounts of suitable dry ingredients were weighed and mixed for 5 min. Next, an alkaline solution was added and mixed for a further 15 min. The alkaline solution was an aqueous solution of 14 molar sodium hydroxide and water glass. The prepared mass was placed in divided molds, six-fold, made of plastic, size 50x50x50 mm and molds size 71x71x71 mm, for each of compositions. The filled molds were compacted on the vibrating table for 3 min. Then, they were placed in a laboratory dryer for 24 h at 75°C. After this time, the samples were cooled to room temperature, removed from molds and stored under laboratory conditions until testing, which was 28 days [13].

2.3. Mix design

For comparative purposes, samples containing 25% and 50% (by weight) of sand were prepared. Then, half of the sand content was replaced with a rubber granules, respectively for both fractions, as shown in Table 3 [13].

<table>
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<th>Table 3. Mix design [13].</th>
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<td>The label of the mix design</td>
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<td>S25</td>
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<td>SG12.5</td>
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<td>LG12.5</td>
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</table>
2.3. Methods

The density of the samples was established using the geometrical method.

The compressive strength test was carried out according with the PN-EN 12390-3 standard, on a MATEST 3000 KM device, on cubic samples 50x50x50 mm.

The abrasion test was carried out according with the PN-EN 1340:2004 standard, on the abrasion tester Böhme. The abrasion measurement machine consists mainly of an abrasive disk. It contains: a rotating disc with a designated abrasive belt, a holder for fixing samples and a burdening device. In each cycle, after mounting the sample to the holder, burdening it and inserting an abrasive on the abrasive belt, the disc was activated, which performed a certain number of rounds. After each cycle, the disc was cleaned and the sample was rotated by 90°. There were executed 16 cycles. The abrasibility after all cycles was calculated as: ΔV - loss of sample volume mm³, using the formula:

\[ \Delta V = \frac{\Delta m}{\rho_R} \]  

The results are given in 1,000 mm³ per 5,000 mm². Abrasion classes were also given according to the mentioned above standard.

3. Results and discussion

3.1. Density

The results of density measurement are presented in Fig. 3.

![Figure 3. Density.](image)

The results of density measurement shows that along with the sand content increase from 25 to 50%, the density increase. Replacing the sand with rubber granules resulted in a decrease in density. The decrease in density was larger with the use of a smaller fraction (0.0 - 0.8 mm) of a rubber granules [13].

3.2. Compressive strength

The results of the compressive strength test are presented in Fig. 4.

![Figure 4. Compressive strength.](image)

The results of the compressive strength test shows that while the sand content increase from 25 to 50%, compressive strength increase. It was observed the addition of rubber granules affected this property negatively. For samples containing 12.5% sand and 12.5% rubber granules, compressive strength values are comparable, regardless of the granules rubber fraction. Compared to samples containing 25% sand, the compressive strength value of samples containing 12.5% sand and 12.5% rubber granules decrease approximately 45%. However, for samples containing 25% sand and 25% rubber granules, a higher value of compressive strength was observed for samples containing rubber granules with a larger fraction (1 - 4 mm). Compared to samples containing 50% sand, the compressive strength value of samples containing 25% sand and 25% rubber granules was reduced approximately 78% and 70%, respectively for the fractions of 0.0 - 0.8 mm and 1 - 4 mm [13].

3.3. Abrasibility

The differences in the height of the samples before and after the abrasion test are presented in Fig. 5. The results of the abrasion test and the abrasion class of samples containing rubber granules are presented in Fig. 6.

![Figure 5. Differences in the height of the samples before and after the abrasion test.](image)

Increasing the sand content from 25 to 50% resulted in a reduction the difference in the height of the samples before and after the abrasion. Replacing part of the sand with rubber granules had a beneficial effect on this prop-
erty. Compared to samples containing 25\% sand, the difference in the heights of the samples before and after the test of samples containing 12.5\% sand and 12.5\% rubber granules decrease approximately 65\%, for both fractions of the rubber granules. Compared to samples containing 50\% sand, the difference in the heights of the samples before and after the test of samples containing 25\% sand and 25\% rubber granules decrease approximately 79\% and 72\%, respectively for the fraction of 0.0 - 0.8 mm and 1 - 4 mm.

![Figure 6. Abrasibility of the samples with rubber granules.](image)

The lowest abrasibility was indicated by a sample containing 25\% sand and 25\% rubber granules with a fraction of 1 - 4 mm. The increased abrasibility was observed for samples with a rubber granules with a smaller fraction (0.0 - 0.8 mm) and with lower content of rubber granules and sand.

4. Conclusions

Based on the results of the conducted tests, it was found that:
- Replacing part of the sand content (by weight) with rubber granules decrease density and compressive strength and increase abrasion resistance.
- The particle size of the rubber granules is significant. Geopolymers with rubber granules with a fraction of 0.0 - 0.8 mm showed lower density. With the content of 25\% of the rubber granules in the geopolymer, the higher compressive strength and the lower abrasibility were exhibited by samples with rubber granules with a fraction of 1 - 4 mm.
- Usefulness of using a rubber granules as a filler in geopolymers based on fly ash. Despite the negative impact of rubber granules on the compressive strength of the obtained material, using it as a filler in geopolymers brings ecological benefits, which include: the possibility of using rubber granules from recycling tires and reducing the consumption of natural raw material such as sand.

**Symbols**

- $\Delta V$  loss of sample volume (mm$^3$)
- $\Delta m$  loss of weight (g)
- $\rho_R$  density of sample (g/mm$^3$)

$h_p$ height of sample before abrasion test (mm)

$h_k$ height of sample after abrasion test (mm)

**References**


