Technogenic Fillers for Epoxy Composites Using Slag of Electric Furnace Steelmaking Production

N Yu Kiryushina¹, A Yu Semeykin²
¹Department of Industrial Ecology, Belgorod State Technological University named after V.G. Shukhov, 46, Kostyukova str., Belgorod, 308012, Russia
²Department of Occupational Safety, Belgorod State Technological University named after V.G. Shukhov, 46, Kostyukova str., Belgorod, 308012, Russia

E-mail: kiryshina.ny@bstu.ru

Abstract. The article presents the results of studies of slag of the Oskol Electrometallurgical Plant (JSC «OEMK») as fillers for epoxy composites. The research data indicate the possibility of using this technogenic product as a filler to increase physical and chemical resistance in the production of composites, which contributes to saving energy resources, waste utilization and improving the ecological situation in the Belgorod region.

1. Introduction

At present, a number of fillers used in the production of epoxy compounds are quite wide. Since the dispersed fillers produced by industry are expensive, the search for new efficient and cheap materials is an actual task. Particularly promising is the use of fillers from technogenic raw materials, which contributes to reducing the anthropogenic load on the environment during waste disposal [1-3].

One of the largest metallurgical plants in Russia – the Oskol Electrometallurgical Plant (JSC «OEMK») is located on the territory of the Belgorod region. The enterprise has introduced a special technology for direct reduction of iron by one-time remelting of iron ore. As a result, the amount of slag increases by two times. At present, over 5 million tons of slag is stored in the dumps of the enterprise [4, 5].

Currently, technological solutions related to the use of of slag-based components for the production of building materials (cement, slagging mixtures, wall blocks) have been developed and are being applied; in road construction (in the composition of asphalt and structural layer of the road base), slag is used as a raw material for the preparation of ultra disperse calcium sulfate dihydrate and colloidal silicic acid, it is a sorbent reagent in the purification of wastewater containing heavy metal ions [6-13].

The aim of the work is the studying of the physical and chemical properties of the slag of OEMK with the possibility of using it as a disperse filler of epoxy compounds.

2. Materials and methods

In this work, slag was used, the chemical composition of which is characterized by an increased content of calcium and magnesium oxides, silica.

The dispersion size of the particles shows that the mass fraction of particles with the optimum particle size (0.003 – 600 μm) is 72.6% (Table 1).
Table 1. Granulometric composition of slag.

| Cell size, mm | 0.6  | 0.4  | 0.22 | 0.06 | 0.003 | <0.003 |
|---------------|------|------|------|------|-------|--------|
| Fraction, %   | 25.2 | 8.0  | 16.6 | 14.2 | 33.8  | 2.2    |

The actual moisture index of the electric steelmaking slag is 0.7 – 0.91%, which meets the requirements of GOST 25592-91. Observance of the moisture content favorably affects the uniformity of mixing, strength properties, and homogeneity [5, 6].

The specific surface of the slag was determined by the adsorption of the methylene blue on the surface of the slag. The specific surface area was 472 m²/kg. It correlates with the values of specific surfaces of previously used fillers [14-16].

The packing density of the particles is characterized by the maximum volume fraction of the dispersed phase and is equal to 0.34 (the ratio of the bulk density is 1120 kg/m³ to the true density is 3300 kg/m³), has sufficiently high values comparable to the known fillers.

To determine the granulometric composition of the fine particle particles, an analysis was made of its dimensionality on a laser particle size analyzer "MicroSizer-201". Fig. 1 shows the percentage of particles of the said granulometric composition in the sample slag being studied.

![Figure 1](image_url)

Fig. 1. Dependence of the weight fraction of slag particles (P, %) on the given particle size values (D, μm).

The shape of the curve indicates the polydisperse composition of the colloidal system. The present maximum fraction of the slag particles is 27.6 μm, which is 12%, the low-dimensional part of the grains from 0 to 10 μm corresponds to 3.37%.

These differences in the nature of particle size distribution affect to the rheological properties, abrasiveness and abrasion resistance, and strength of the material.

The chemical composition of the slag is shown in Table 2.

Table 2. Chemical composition of slag.

| Chemical composition, % |
|-------------------------|
| CaO         | 54.80 |
| SiO₂        | 25.58 |
| Al₂O₃       | 7.15  |
| FeO         | 1.7   |
| MnO         | 0.82  |
| MgO         | 9.81  |
| Cr₂O₃       | 0.07  |
| Mo          | 1.9   |
3. Results and discussion

The results of the determination of the chemical composition of the slag indicate that it consists of minerals widely used as disperse fillers in polymers and it is suitable for use in composites.

Thus, the research data indicate the possibility of using this technogenic product as a filler to increase physical and chemical resistance in the production of composites, which contributes to saving energy resources, waste utilization and improving the ecological situation in the Belgorod region.

In the development of epoxy compositions of low combustibility, epoxy resin ED-20, plasticizer dibutyl phthalate (DBP), the hardening agent polyethylene polyamine (PEPA), filler – slag fraction <0.315 mm – were used. Because PEPA has a non-constant chemical composition, the hardening agent content was selected based on the results of the curing kinetics of the epoxy matrix. The main parameter of choice is the preservation of the degree of cure. The optimum value of the hardening agent is 10% (Fig. 2, Table 3).

![Figure 2. Kinetics of curing of epoxy compositions of composition, mass parts: 1 – 70 ED-20 + 30 DBP + 6 PEPA; 2 – 70 ED-20 + 30 DBP + 10 PEPA; 3 – 70 ED-20 + 30 DBP + 10 PEPA + 0,5 mass parts of slag; 4 – 70 ED-20 + 30 DBP + 10 PEPA + 25 mass parts of slag.](image_url)

It was also found that the electric steel melting slag incorporated in the epoxy composition in an amount of 0.5 mass parts is a structure-forming agent; it reduces the gel time of the material from 80 minutes to 50 minutes and reduces the maximum curing temperature from 126 to 110 °C. Slag, introduced in an amount of 25 mass parts, leads to increasing of the curing temperature (Figure 2), and exhibits the properties of the active filler.

**Table 3.** Degree of cure of epoxy composites containing 70 mass parts of ED-20 and 30 mass parts of DBP.

| Amount of PEPA and slag, mass parts | Degree of cure, % (24 hour) |
|------------------------------------|-----------------------------|
| 6 PEPA                             | 74                          |
| 8 PEPA                             | 77                          |
| 10 PEPA                            | 81                          |
| 10 PEPA + 0,5 slag                 | 80                          |
| 10 PEPA + 25 slag                  | 73                          |
| 10 PEPA + 30 slag                  | 67                          |
Mathematical processing of the results of the experiments made it possible to establish parameters for optimizing the production of epoxy compositions of low combustibility [17-20]. Polynomial models describing the process of curing the epoxy composition in the presence of electric steelmaking slag as a function of the process time are obtained:

For the composition 1:
\[ y = 2 \times 10^{-2} x^5 - 9 \times 10^{-5} x^3 + 2 \times 10^{-5} x^2 - 0.0015 x + 0.0574 x^2 - 0.6711 x + 22.316 \]

For the composition 2:
\[ y = -3 \times 10^{-10} x^5 + 2 \times 10^{-5} x^3 - 4 \times 10^{-5} x^2 + 0.0045 x^3 - 0.1883 x^2 + 2.976 x + 24.965 \]

For the composition 3:
\[ y = -3 \times 10^{-10} x^5 + 2 \times 10^{-5} x^3 - 4 \times 10^{-5} x^2 + 0.0034 x^3 - 0.1208 x^2 + 1.4747 x + 28.445 \]

For the composition 4:
\[ y = 2 \times 10^{-10} x^5 - 1 \times 10^{-5} x^3 + 2 \times 10^{-5} x^2 - 0.0011 x^3 + 0.0172 x^2 + 0.3422 x + 17.96 \]

The root-mean-square values of the reliability of the approximation were, respectively: for the composition 1 \( R^2 = 0.9378 \), for the composition 2 \( R^2 = 0.9401 \), for the composition 3 \( R^2 = 0.8961 \), for the composition 4 \( R^2 = 0.9078 \).

4. Conclusion

The use of technogenic wastes of the metallurgical industry in various industries is a promising way to reduce the environmental burden in the Belgorod region and other regions of the Russian Federation. The possibility of using OEMK slag as a filler for epoxy composites is theoretically justified and proved experimentally. It is shown that the chemical composition of OEMK slag meets the requirements for fillers of composites based on epoxy binder. The electric steel-smelting slag introduced into the epoxy composition in an amount of 0.5 mass parts exhibits the properties of the active filler, reduces the gel time and the maximum curing temperature of the composition.

5. References

[1] Purohit A, Satapathy A 2017 Mechanical and wear characteristics of epoxy composites filled with industrial wastes: A comparative study *IOP Conference Series: Materials Science and Engineering* **178** (1) 0120196
[2] Bărbuță M, Țăranu N, Harja M 2009 Wastes used in obtaining polymer composite *Environmental Engineering and Management Journal* **8**(5) 1145-1150
[3] Das B, Prakash S, Reddy P S R, Misra V N 2007 An overview of utilization of slag and sludge from steel industries *Resources, Conservation and Recycling* **50**(1) 40-57
[4] Kiryushina N Yu, Tarasova G I, Sverguzova S V 2010 Slag waste in water treatment *Bulletin of BSTU named after V.G. Shukhov* **4** 140–145
[5] Shapovalov N A, Zagorodnyuk L Kh, Tikunova I V, Schekina AYu, Shkarin A V 2013 Slags of metallurgical production – an effective raw material for obtaining dry construction mixtures *Fundamental research* **1**(1) 167–172
[6] Lupandina N S, Kiryushina N Yu, Porozhnnyuk E V 2017 Extension of Raw Material Base for Ceramic Building Bricks Production *Solid State Phenomena* **265** 352–358
[7] Lupandina N S, Saponova Zh A 2012 *Sewage purification from heavy metals by production wastes of bioses* (Belgorod: BSTU named after V.G. Shukhov)
[8] Santamaria A, Roji E, Skaf M, Marcos I, González J J 2016 The use of steelmaking slags and fly ash in structural mortars *Construction and Building Materials* **106** 364-373
[9] Sverguzova S V, Porozhnuyk L A, Ipanov D Y, Shamshurov A V, Novikova E V 2013 Colloid chemical Properties of Electric Arc Furnace Dusts in Processes of Wastewater Treatment *Ecology and Industry of Russia* **7** 22-25
[10] Kiryushina N Yu 2013 Peculiarities of Purification of Wastewaters of Electroplating Industries from Ions of Heavy Metals by the Slag of Electric Furnace Steelmaking *Water Treatment* **6** 44-58
[11] Sverguzova S V, L A Porozhnuyk, Sukhanov E V, Fomina E V, Denisova L V, Shaihiev I G
2016 Some of the features of coagulation treatment of water using a dust of electric steel production *Bulletin University of technology (KNRTU)* 19(9) 158-163

[12] Vasilenko T A, Koltun A A 2017 Chemical Aspects of the Obtaining of Iron-Containing Coagulant-Floculant from Electric Steel Melting Slag for Wastewater Treatment *Solid State Phenomena* 265 403–409

[13] Sverguzova S V, Starostina I V, Sukhanov E V, Sapronov D V 2016 Influence of modification of the dust of electric steel production on its coagulation properties *Bulletin University of technology (KNRTU)*, 19(3) 113-115

[14] Guzel G, Deveci H. 2018 Properties of polymer composites based on bisphenol A epoxy resins with original/modified steel slag 39(2) 513-521

[15] Guzel G, Deveci H 2017 Physico-mechanical, thermal, and coating properties of composite materials prepared with epoxy resin/steel slag Polymer Composites 38(9) 1974-1981

[16] Biswas S, Satapathy A 2010 Use of copper slag in glass-epoxy composites for improved wear resistance *Waste Management and Research* 28(7) 615-625

[17] Gordienko M, Kruchinina N, Kuzin E, Vovynskiy A 2012 Process Optimization of Obtaining Solidified Forms of Alumosilicic Flocculant-Coagulant for Application In Wastewater, *Bezopasnost v tekhnosfere*, 1(4) 21-25

[18] Gordienko M G, Kuzin E N, Vovynskiy A A, Nadeeva E N 2012 Mathematical methods of the analysis in the course of optimization of drying aluminium-silicate flocculate-coagulant *Bulletin of the Saratov State Technical University* 64 175-180

[19] Semeykin A Yu, Tikhomirova K V 2015 Modeling of functional parameters of electrically conductive composites based on Portland cement and carbon materials *Youth and scientific and technical progress: Proceedings of VIII International Scientific and Practical Conference* vol. 3 (Stary Oskol: Ltd «Assistant Plus») 241-245

[20] Goncharova M A, Komarichev A V, Maklakov S V, Karaseva O V 2017 Optimizing the composition of magnetic polymer sealing composites with the application of slag ferromagnetic filler *Journal of Chemical Technology and Metallurgy* 52(4) 636-641

**Acknowledgments**

The work is realized in the framework of the Program of flagship university development on the base of the Belgorod State Technological University named after V.G. Shukhov, using equipment of High Technology Center at BSTU named after V.G. Shukhov.