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## ENHANCING MECHANICAL PROPERTIES OF COMPOSITE POLYMER CONCRETE WITH LANTHANUM OXIDE ADDITIVE FOR POTENTIAL USE IN ANTI-RADIATION APPLICATIONS

Polymer concretes constitute a commonly used group of materials with known and well-studied properties for construction applications. The following research is a preliminary investigation into the basic mechanical properties and structure of a proposed novel polymer concrete with a lanthanum oxide nanopowder additive. The composite material is made from epoxy resin binder with milled expanded clay filler and  $\text{La}_2\text{O}_3$  nanopowder. The research samples were made by simple and scalable casting methods. The conducted mechanical testing included compression and flexural examinations typical for this group of materials, as well as Brinell hardness measurements. The microstructure of the manufactured samples was examined utilizing scanning electron microscopy supported by EDS analysis. The obtained results reveal acceptable mechanical properties for the investigated materials, with slight increases in the measured property values for increasing amounts of the nanoparticle addition. The SEM and EDS investigations show the dispersion of filler and nanopowder additive throughout the samples, which is advantageous for the macroscopic properties of the material. The slight agglomeration of the lanthanum oxide powder could be further decreased with the inclusion of another processing step, for example, resin mixture sonication. The mechanical properties of the investigated materials are adequate and further research is suggested to test the possibilities of developing the examined polymer concrete for anti-radiation and radiation shielding applications.

**Keywords:** polymer concrete, composite, lanthanides, anti-radiation, mechanical properties

### INTRODUCTION

Polymer concretes constitute a group of materials most commonly defined as composite materials similar to concrete, in which standard cement binders have been replaced by polymers [1, 2]. The replacement of conventional binders with polymeric material has significant advantages, examples of which are: heightened environmental and chemical resistance, increased mechanical properties, and multifunctionality resulting from the possibility of using various binders and fillers [1]. Through the last few decades, polymer concrete has seen plenty of use in industry [1-3] and numerous studies have been carried out to examine the mechanical properties of polymer concretes, with different polymer binders, various fillers, and changes to their amounts as well as modifications to the curing conditions [3-13]. Besides typical mechanical properties, the testing of polymer concrete durability and resistance to environmental influences has also been performed [14]. Advanced polymer concrete research includes materials that have been strengthened under the influence of radiation [15] and composites with nanomaterial reinforcement [16]. More recent investigations expand upon using polymer concrete with recycled and waste materials [17-22]. Experiments with polymeric waste [17], fly

ash [18], recycled PET [19], CRT glass waste [20], textile waste [21], and automotive glass [22] used as fillers show promising results that could lead to the examined materials becoming another way of dealing with waste difficult to recycle or to more environmentally friendly construction materials. Polymer concretes could also provide an effective and viable solution in more advanced applications – with the addition of functional materials like nanoparticles of certain types. Examples could include radiation shielding, anti-bacterial, and more, depending on the used nanopowder filler.

Lanthanum oxide has recently seen a great deal of interest as a material for anti-radiation applications [23-25]. Research has been conducted into using  $\text{La}_2\text{O}_3$  as an additive in composite materials, with promising results, yet to our knowledge, there have been no significant attempts to incorporate lanthanum oxide into polymer concrete-type materials. Polymer concrete with an  $\text{La}_2\text{O}_3$  addition could provide an interesting and cost-efficient alternative to conventional construction materials for advanced applications like radiation shielding. If proven to be effective, such a material would be possible to use in nuclear power plants and other demanding environments.

This paper aims to provide a preliminary investigation into the influence of a functional nanopowder addition to polymer concrete. To consider the future application of such a material, it is crucial to examine and ensure that the researched additives have no negative consequences on the mechanical properties of the material, starting with small amounts of the additive.

## METHODOLOGY

Samples were prepared by mixing the Epidian 6 epoxy resin system (Ciech, Poland) with an expanded clay aggregate filler milled with an SK300 cross beater mill (Retsch, Germany) and  $\text{La}_2\text{O}_3$  nanopowder purchased from Merck (Germany). The mixed materials were then degassed using a vacuum pump to prevent porosity. After that, the Z-1 curing agent was added to the resin and the samples were left to cure. The examined sample series contained 0 (control group), 0.5, 1, and 2 weight percent additions of  $\text{La}_2\text{O}_3$  nanopowder. Mechanical testing was carried out by means of an Instron 4469 universal testing machine (Instron, USA) with a 5 kN load and 5 mm/min loading velocity. Hardness measurements were made with a Brinell hardness tester HK460 (Heckert, Germany) under 365 N load. SEM examination was conducted utilizing a Phenom Pro X desktop scanning electron microscope (ThermoFisher, USA). Data curation was carried out with Origin software (OriginLab, USA). The sizes of the samples for the conducted investigations are presented in Figure 1.

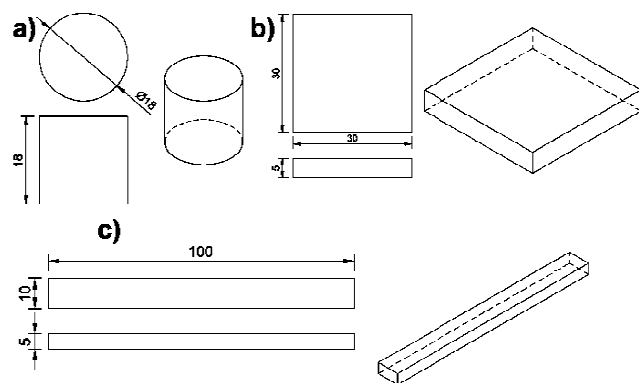


Fig. 1. Sample size comparison (in millimeters): a) samples for compression test, b) samples for flexural test, c) samples for hardness testing

## RESULTS AND DISCUSSION

### Compression testing

Compression tests were carried out on a series of three samples for each examined material. The resulting averaged curves are presented in Figure 2.

As can be seen in Figure 2, the presence of the nanopowder in the composite material increases the compressive strength, although the increase is slight. In comparison to typical compressive strength values re-

ported in the literature, the mechanical properties of the examined material land within the range expected from polymer concrete materials. Taha et al. made a comparison of polymer concretes with compressive strengths from around 60 to 180 MPa [1], therefore placing the strength of our polymer concrete near the lower range of typically acceptable compressive parameters. Since the intended application described in this research involves specialized elements which will most likely bear less weight and stress than typical construction material, the values in the range of conventional polymer concrete are highly advantageous and promising for further research.

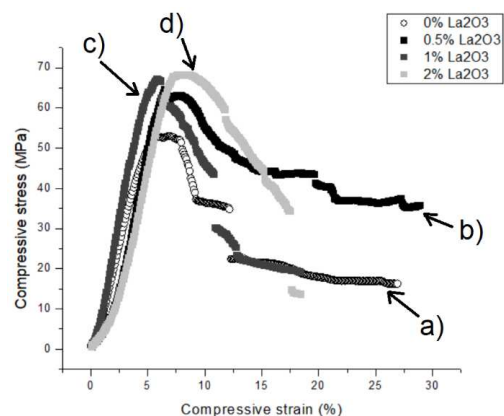


Fig. 2. Average compression test curves for examined sample series: a) control group sample (white circles with black border), b) 0.5 wt.%  $\text{La}_2\text{O}_3$  addition (black curve), c) 1 wt.%  $\text{La}_2\text{O}_3$  addition (dark gray curve), d) 2 wt.%  $\text{La}_2\text{O}_3$  addition (light gray curve)

### Flexural testing

The average flexural stress/strain curves achieved during the investigation are shown in Figure 3.

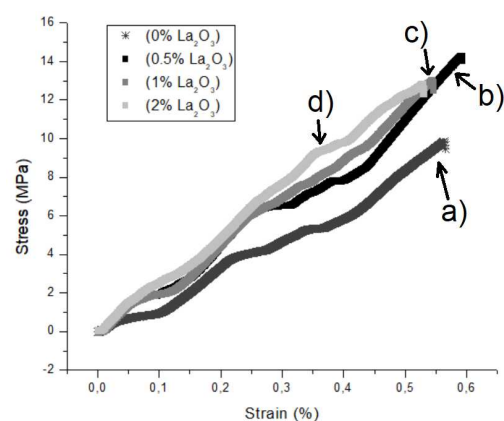


Fig. 3. Average three-point bending test curves for examined sample series, a) control group sample (bottom dark gray curve), b) 0.5 wt.%  $\text{La}_2\text{O}_3$  addition (black curve), c) 1 wt.%  $\text{La}_2\text{O}_3$  addition (gray curve), d) 2 wt.%  $\text{La}_2\text{O}_3$  addition (light gray curve)

The measured flexural strength shows differences between the control group material and the samples with the nanopowder addition. For the examined polymer concretes, there is a significant increase in flexural

strength, with the highest value up to 14.3 MPa for the samples with the 0.5 wt.%  $\text{La}_2\text{O}_3$  addition, and 13 and 12.8 MPa for the 1 and 2 wt.%  $\text{La}_2\text{O}_3$  samples, respectively. Despite a noticeable increase in the strength of the material with the nanopowder additive in comparison to the control group samples, there is seemingly little difference in the flexural parameters between each composite material sample series. In comparison to existing research, some reports [7] show results of around 10 MPa for polymer concrete flexural strength, while more comprehensive literature places typical values in the range from 14 to 28 MPa [1], with more experimental research achieving higher flexural strength [20, 21]. With values of 13 to 14 MPa, the investigated material exhibits acceptable properties.

**Hardness measurements**

The hardness measurement results are presented in Figure 4.

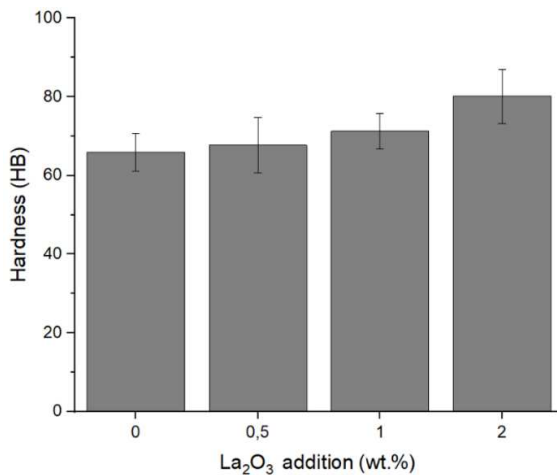


Fig. 4. Average hardness values for examined sample series

TABLE 1. Values and standard deviations for examined sample series

Wt.% addition of $\text{La}_2\text{O}_3$	Hardness [HB]	SD
0	65.9	4.7
0.5	67.7	7.0
1	71.3	4.5
2	80.1	6.9

While the difference in the hardness values could be noticed in Figure 4, it is important to consider that almost all the reported hardness test results lie within one another's standard deviation range. Only in the material with the 2 wt.% addition of  $\text{La}_2\text{O}_3$  can the hardness result be reliably assumed to be higher than in the control group sample series average. The measured Brinell hardness values fall within a 65 to 80 HB range, which is expected for the used epoxy binder and amounts of filler. The results point to a small but potentially insignificant rise in hardness with increasing amounts of additive nanoparticles. The achieved results are a such

probably due to the small amount of nanopowder used, in which case, the greatest influence on the hardness comes from the epoxy resin matrix and the expanded clay filler properties.

**SEM examination**

SEM micrographs of the examined polymer concrete material are presented in Figures 5 and 6. The magnification and the applied examination modes can be seen on the marker for each respective micrograph in Figures 5 and 6. The samples for the SEM investigation were cut through the middle, with the intent to check for potential segregation of the filler and nanoparticle additive in the sample. The micrographs presented in Figures 5 and 6 were taken roughly from the center of the sample cross-section.

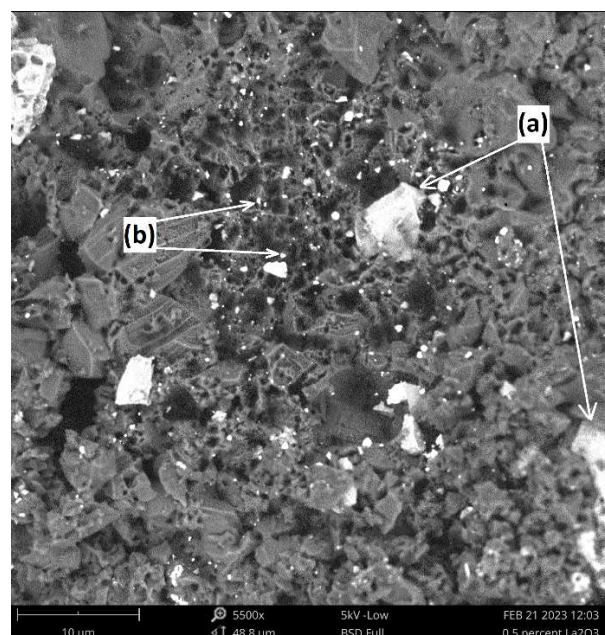
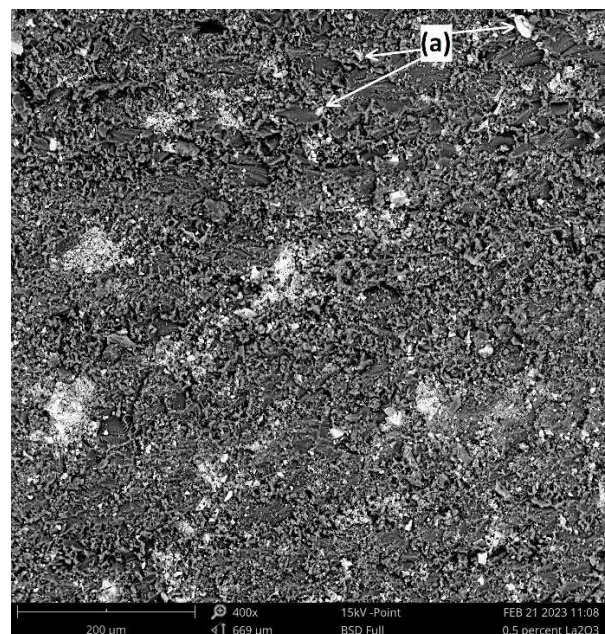


Fig. 5. SEM micrographs of sample with 0.5 wt.% addition of  $\text{La}_2\text{O}_3$

The top micrograph in Figure 5 shows the sample cross-section morphology, with a dark grey epoxy matrix with lighter dispersed expanded clay particles and grain-like agglomerates – a in Figure 5. The achieved filler dispersion is satisfactory. In the bottom micrograph, small, white particles of  $\text{La}_2\text{O}_3$  powder can be seen between the larger expanded clay pieces – b in Figure 5. Small amounts of  $\text{La}_2\text{O}_3$  correspond to the intended volume of the sample (0.5 wt.% addition).

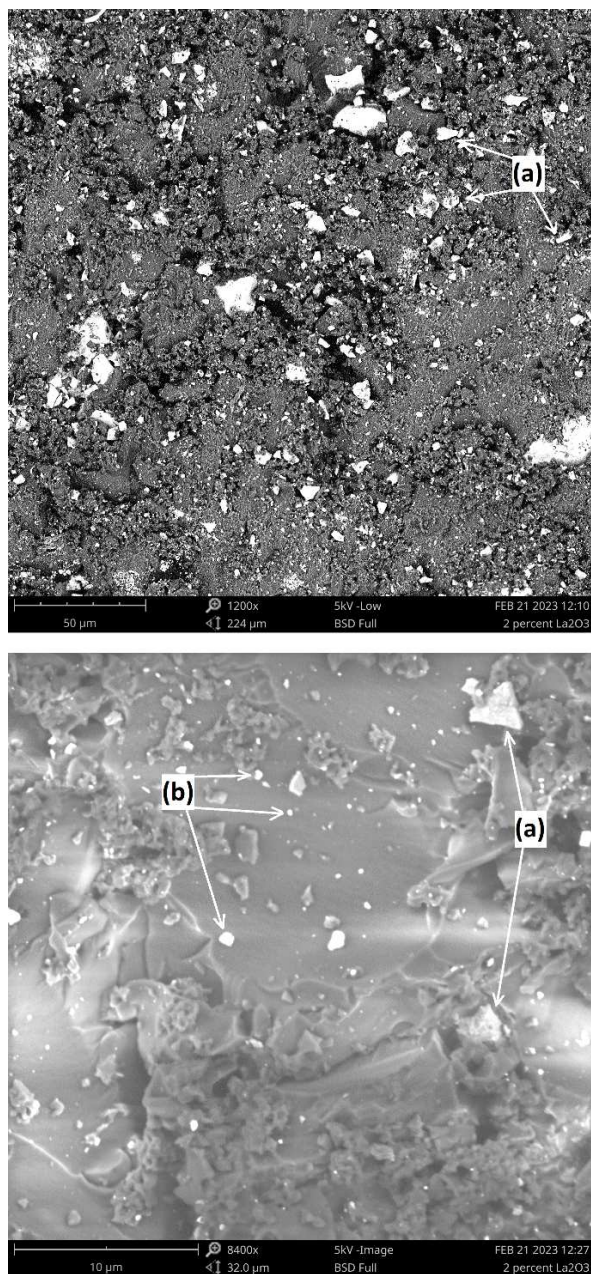


Fig. 6. SEM micrographs of sample with 2 wt.% addition of  $\text{La}_2\text{O}_3$

Figure 6 displays examples of micrographs for the samples with the 2 wt.% addition of lanthanum oxide. In the top micrograph, the morphology of the cut cross-section of the polymer concrete sample can be seen. The dark grey epoxy matrix is sprinkled with lighter expanded clay particles mixed into the resin (shown in a). The milled expanded clay grains sizes are within

the 20 to 50  $\mu\text{m}$  range. In the bottom micrograph, smaller agglomerates of  $\text{La}_2\text{O}_3$  nanoparticles can be seen as white granules, with sizes around 2  $\mu\text{m}$  and lower (b). In comparison to the sample with 0.5 wt.%  $\text{La}_2\text{O}_3$  added, a larger amount of nanopowder additive can be seen, while the morphology of the sample remains roughly the same, with relatively well-dispersed expanded clay filler in the epoxy matrix.

To prove the presence of the nanoparticles and their proper dispersion in the manufactured samples, EDS examination was performed as qualitative analysis, with a result example shown in Figure 7.

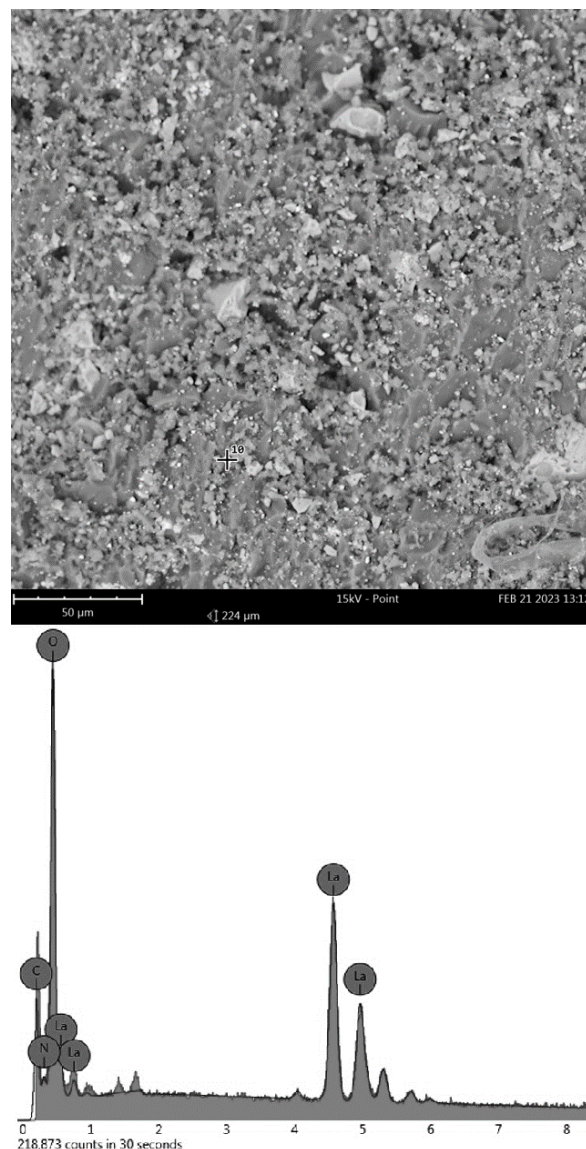


Fig. 7. Example of EDS examination result (single point scan) from sample with 2 wt.% addition of  $\text{La}_2\text{O}_3$ , showing presence of  $\text{La}_2\text{O}_3$  nanopowder agglomerates distributed within sample structure

The noticeable  $\text{La}_2\text{O}_3$  particle presence in the cross-section of the sample center has been confirmed.  $\text{La}_2\text{O}_3$  is distributed throughout the sample without larger segregation in specific sections of the examined sample, which is significantly advantageous for the material; however, the nanopowder used in the composite still

suffers from agglomeration, typical for the applied manufacturing method (casting). Lanthanum oxide particle agglomerates can be seen in the micrograph in Figure 7 as small, round, white, grain-like dots and specks, of sizes below 5  $\mu\text{m}$ . Further improvements in powder dispersion could be made by the inclusion of additional processing steps, for example, sonication treatment of the mixture before casting; nevertheless, deagglomeration to a such extent might not be necessary for this type of material and its application, which will be investigated in the future.

## CONCLUSIONS

The addition of nanopowder to polymer concrete-type materials increases the mechanical properties, as seen in the results from the compression and three-point bending tests. The most significant increase can be seen for the compressive strength, though the examined materials do not stand out in comparison to conventionally used and investigated polymer concretes. The flexural strength increases slightly compared to the control group material, whereas the hardness change falls mostly within the standard deviation range between the examined sample series. This may result from the synergistic interactions between the micro and nano powder. While the increase in the mechanical properties is not as great as in comparable research, it must be noted that with the used amounts of nanopowder, the achieved results are more significant, especially considering the fact that the further supposed application of the proposed material does not demand higher mechanical properties than those obtained in this investigation. Overall, the preliminary mechanical properties examination gives promising results, and further research could be carried out to examine the functional properties of polymer concrete with  $\text{La}_2\text{O}_3$  additions for further development of the material for its suggested application.

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