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Possibility of using recycled cathode ray tube (CRT) glass as filler source in polymer epoxy composites: effect of glass content and modification on mechanical strength and leaching behaviour

Możliwość wykorzystania szkła kineskopowego (CRT) pochodzącego z recyklingu jako wypełniacza w kompozytach polimerowo-epoksydowych: wpływ zawartości i modyfikacji szkła na wytrzymałość mechaniczną i zachowanie podczas wymywania

This paper investigates the possibility of using waste cathode ray tube (CRT) glass derived from discarded e-waste as an alternate filler for polymer composites. Most of proposed technologies for recycling CRT glass are energy-consuming and some of them allow for use of only a limited quantity of waste glass. The method proposed in this paper offers the use of ecological and low energy consuming technology of preparing polymer composite filled with waste CRT glass as filler. Epoxy matrix composites were prepared with different loads of finely ground (<90 µm particle size) waste CRT glass cullet. Apart from this filler was subjected to additional surface modification with organofunctional silane to enhance adhesion between polymer matrix and glass filler. Physical, mechanical, and durability properties, lead leachability, and influence of silane modification on lead immobilization was studied. The results show that it is possible the use waste CRT glass as filler for epoxy composites. Composites with good mechanical properties were obtained. Utilization of this type of epoxy composite is an effective way for immobilization of lead included in CRT glass; additional modification with aminosilane coupling agent allows for reduction of Pb leachability from 300 mg/l to 0.01 mg/l.

Keywords: *polymer composite, cathode ray tube (CRT), recycling, leaded glass, filler*

W artykule przedstawiono wyniki badań nad możliwością wykorzystania odpadowego szkła kineskopowego (CRT) pochodzącego ze zużytych elektroodpadów jako alternatywnego wypełniacza do kompozytów polimerowych. Większość proponowanych technologii recyklingu szkła kineskopowego jest energochłonna, a niektóre z nich pozwalają na wykorzystanie jedynie ograniczonej ilości szkła odpadowego. Zaproponowana w artykule metoda umożliwia wykorzystanie ekologicznej i niskoenergochłonnej technologii wytwarzania kompozytu polimerowego z odpadowym szkłem ołowiowym CRT jako wypełniaczem. Kompozyty z osnową epoksydową przygotowano z różnymi zawartościami drobno zmielonej (<90 µm wielkości cząstek) odpadowej stłuczki szklanej CRT. Dodatkowo wypełniacz poddano modyfikacji powierzchni organofunkcyjnym silanem w celu zwiększenia przyczepności pomiędzy matrycą polimerową a wypełniaczem szklanym. Badano właściwości fizyczne, mechaniczne, wymywanie ołowiu z kompozytów oraz wpływ modyfikacji silanem na immobilizację ołowiu w kompozytach. Wyniki pokazują, że możliwe jest wykorzystanie odpadowego szkła CRT jako wypełniacza do kompozytów epoksydowych. Otrzymano kompozyty o dobrych właściwościach mechanicznych. Zastosowanie tego typu kompozytu epoksydowego jest skuteczną metodą immobilizacji ołowiu zawartego w szkle CRT; dodatkowa modyfikacja aminosilanowym środkiem sprzęgającym pozwala na zmniejszenie wymywalności Pb z 300 mg/l do 0,01 mg/l.

Słowa kluczowe: *kompozyty polimerowe, szkło kineskopowe, recykling, szkło ołowiowe, wypełniacz*

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1. Introduction

Industrial waste is a hazard both in its production, transport, and disposal. If improperly managed, they may affect all components of the environment. These wastes are characterized by various properties and degrees of pollution, depending on the source of origin and the technology used. Knowledge of the composition and chemical properties of waste determines the way of its management. The most desirable direction is reuse through recirculation or use in other industries. However, not all waste can be managed in this way or it is economically unprofitable. Therefore, waste is subjected to landfill, even though it is the final and least preferred direction of management. Waste management or neutralization can take place in various ways, the most common being deposited in landfills.

2. Theory

The withdrawal from the use of technologically obsolete TV sets and CRT (cathode ray tube) monitors gave rise to the problem of their management and recycling. However, this issue is problematic due to the diverse nature of the waste such as waste cullet glass, the heterogeneity of its composition, and the content of elements harmful to the environment such as lead, cadmium, barium, strontium [1–9].

The most widely proposed use of cullet from CRTs are various products used in construction. Examples of such products are ceramic-glass composites, traditional ceramics, aggregates in concrete and cement, and others. Waste glass cullet is used as an alternative filler in the production of ceramic-glass composites [1–4]. Such composites are made of finely ground waste glass and other industrial waste (fly ash, mine waste, solid waste from aluminium smelting, dolomite).

Ecologically hazardous materials, such as waste glass cullet and fly ash from coal-fired power plants, were used to create porous glass-ceramics. The method of waste glass recycling proposed by Mangutova et al. [2] was based on the creation of a ceramic-glass composite on a polyurethane matrix in the high-temperature heating process at the temperature of 1423 K. Pre-prepared with polyurethane matrix waste glass was homogenized with fly ash in planetary mills before the firing process. During the firing process, the polyurethane skeleton burned down, leaving behind glass-ceramic material. A similar methodology was used by Andreola et al. [10]: ceramic-glass composites were obtained from cullet from the panel and funnel of a color CRT TV set, as well as dolomite and aluminum oxide used as stabilizers.

Traditional ceramics also found application in the recycling of CRT glass waste glass cullet. Dondi, Loryuenyong, and Raimondo [11–13] describe the possibility of its creation on the basis of clay with finely ground waste glass as a filler. There are also proposed solutions for the use of finely ground glass cullet as aggregates in cement and concrete [14–16], cement produced with the addition of powdered glass does not have different properties than cement without the addition of this filler [17].

Polymer composites are a more ecological solution due to the energy efficiency of the process. Research on chemical-resistant linings with the use of CRT glass [18] or as a filler for thermoplastic polymers such as polypropylene [19] and polymer concretes [20].

The subject of the present research was the development of polymer composites filled with waste filler (grain size <90 μm) coming from ground CRT glass. Unmodified waste glass and bulk-modified glass with the addition of amino-functional silane were used, for which it was expected to obtain an improvement in mechanical parameters due to stronger interaction at the glass/polymer matrix interface.

It should be mentioned that in the normal production process of glass fillers, e.g. glass fibers, the surface modification process with coupling agents takes place immediately after the production of the glass fiber. The modification process is carried out from an aqueous solution containing technological additives such as emulsifiers, lubricants and coupling agents, which promotes even coverage of the filler with a layer of coupling agent and the formation of a hydrophobic layer on the glass surface, and is also the most effective method of modification of the glass surface with coupling agents [21]. Due to the fact of using recycled glass in the research, the addition of aminosilane was introduced directly into the polymer resin. A 2-component epoxy resin was used as the matrix of the composites.

The utilization of waste CRT glass by the production of polymer epoxy composites has a significant advantage in relation to the methods proposed above: high degree of filling of polymer matrix and low-temperature process with low energy requirements. The content of the filler, which is the finely ground waste CRT glass cullet, is in the range of 50–75% by weight (up to 35% by volume) in the case of composites intended for casting. The values of the maximum glass content were determined on the basis of casting tests.

Application of waste CRT glass as raw materials in newly developed technologies requires ensuring not only appropriate performance parameters of such products but also an appropriate level of their safety. The mobility of pollutants released from waste and composite material was determined and expressed as the result of the leaching process. The study assessed also the influence of waste powder fillers on the mechanical properties of polymer composites, which may determine their future applications.

3. Materials and methods

3.1. Materials

CRT glass came from the CRT glass recovery installation operated by PW Ekotop Renata Kazibudzka (Częstochowa, Poland). Waste filler was delivered from a waste processing plant in the form of glass cullets with a grain size greater than 3 mm. Cathode ray tube glass with a particle size >3 mm was ground to a glass powder with a particle size <1 mm using a disintegrator mill. A disk-and-pin mill, belonging to the group of rotor-type comminution devices with a through-flow action, was used. It was equipped with two parallel disks (one movable and one stationary) with several rows of steel pins arranged concentrically on each disk. In the final stage, the ground material was screened through a 1 mm mesh sieve, after grinding the material, the degree of fragmentation was checked by sifting it through a 1 mm sieve, the residue on a 1 mm sieve was 0%. For characterizing the cathode ray tube glass in its solid form and its physicochemical properties, a fraction below 200 μm was used, which was obtained by screening the ground glass with

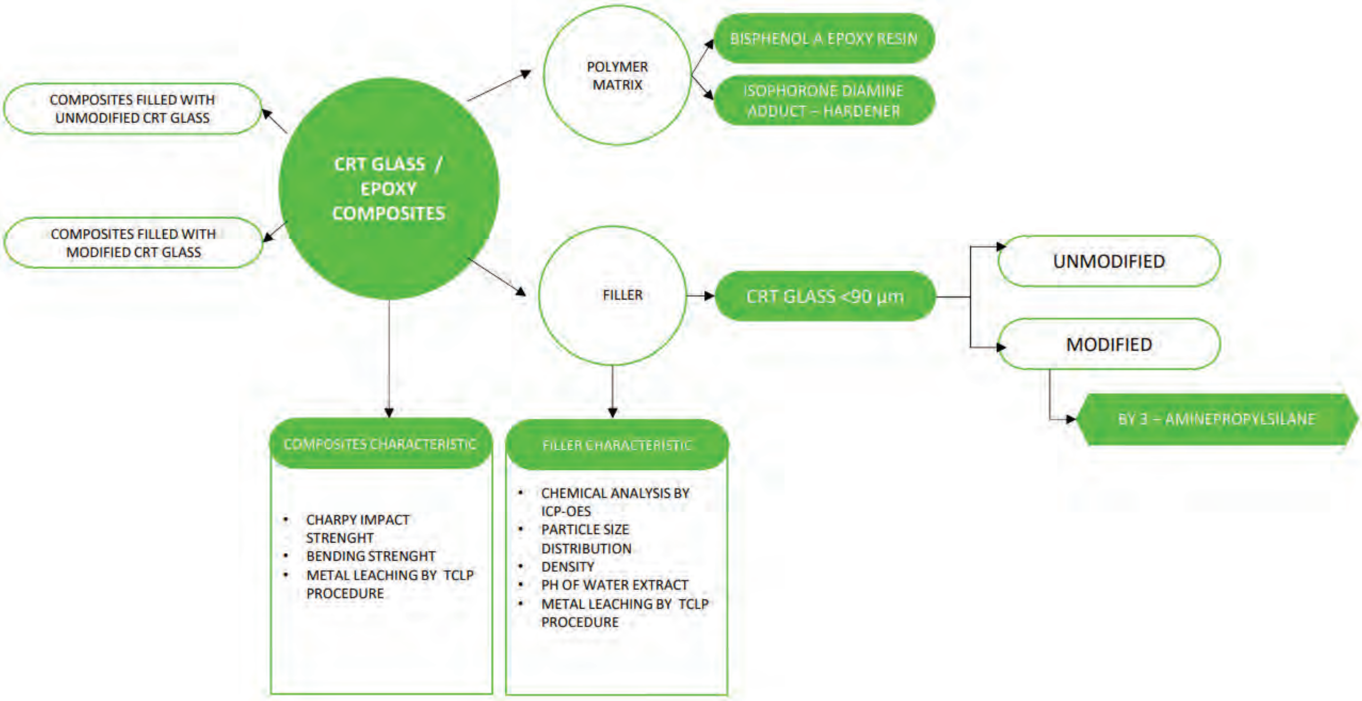

Fig. 1. Research scheme

Rys. 1. Plan badań

a granulation below 1 mm through a 200 µm sieve. Due to the excessive particle size that could significantly reduce the strength properties, a fraction <90 µm was selected for composite production based on preliminary trials. This finer fraction was obtained by further screening the <200 µm fraction through a finer sieve.

The polymer matrix was epoxy resin Epidian 601 (CIECH Sarzyna) which was a reaction product of bisphenol A with epichlorohydrin with cresyl glycidyl ether as a reactive diluent. According to the producer data resin has an average molecular weight ≤700, epoxy number of 0.50–0.55 mol/100 g. Epidian 601 contains an active diluent that gives the resin a low viscosity, which facilitates the addition of fillers in the form of a powder. It was assumed that the epoxy resin used as a polymer matrix of the composite containing mineral fillers should have a pourable consistency and low viscosity, the possibility of casting and cross-linking at ambient temperature, and chemical resistance. The cross-linked composition should be resistant to acids and their dilute solutions due to the possibility of using the materials in external conditions in which they will be leached.

Cross-linking of epoxy compositions filled with waste glass was carried out using the IDA hardener (CIECH Sarzyna) dedicated for Epidian 601. Hardener based on the cycloaliphatic polyamine adduct – isophorodiamine (>25% by weight) with amine value 200–350 mg KOH/g. The research scheme shows Fig 1.

3.2. Waste filler characterization

Powdered CRT glass is characterized by chemical analysis by ICP--OES method, physical properties, particle size distribution, and optical microscopy. The actual density of fillers was determined by the pycnometric method at 25°C according to EN ISO 787-10 standard: General Methods for Testing Pigments and Fillers – Density Determination – Pycnometric Method. The test was performed according to method A, consisting of weight determination of the mass of the sample in a Gay-Lussac pycnometer at a temperature of 23°C in the presence of air and a displacement liquid. The displacement liquid for the test was distilled water and ethanol p.a. (used to determine the density of the displacement liquid).

The preparation of solid samples for the chemical composition tests was carried out by microwave mineralization in a closed pressure system, in a system of concentrated mineral acids: HNO_3 + HF. Fluoride ions were bound in a separate mineralization cycle with boric acid H_3BO_3.

The chemical composition of the filler was determined by induced plasma optical emission spectrometry (ICP-OES) using a Thermo Scientific iCAP 700 Duo spectrometer. Measurement of the intensity of the emitted radiation with wavelengths characteristic for the studied elements in the obtained mineralizates was carried out using the optical emission spectroscopy technique (ICP-OES) with the use of appropriate background correction. Glass samples were analyzed for the presence of the following elements: Al, Ba, Ca, Fe, Mg, Sr, S, Ti, Zr, Pb, Zn, Cd, Co, Cu, Ni, Cr, Mn, V, Mo, As, and Sb.

The particles size distribution of the filler-CRT glass was investigated by laser diffraction. The study was carried out on the NanoTec Analysette 22 (Fritsch). The test was carried out using the wet method in a dispersing medium, i.e. distilled water. According to the Fraunhofer theory, for calculations, the measuring range was adopted from 0.10 µm to 504 µm. The device uses light diffraction to determine the grain size distribution. In a parallel laser beam, the particles scatter light at angles that depend on the particle diameter. Using comprehensive mathematical methods, the size distribution is calculated from the intensity of the scattered light. The average volumes of the hypothetical spherical particles are measured, from which their theoretical diameters are calculated, and the resulting particle size distribution is the volumetric distribution. Epoxy-glass composites were produced with the use of cullet waste from cathode ray tubes, which were characterized during the above-mentioned tests of the filler properties.

3.3. Composite preparation

The epoxy glass composites were prepared by adding a specified amount of filler into the liquid epoxy resin. Series of composites were prepared with the addition of unmodified glass and with modification with an adhesion promoter. Composites were prepared with the following filler contents of 10%, 20%, 25%, 35% by volume. According to the recommendations of the manufacturer, the epoxy resin with the hardener was mixed according to the weight ratio of 100 : 50.

One series of composites was prepared with the addition of a coupling agent, which was supposed to improve the adhesion between the polymer matrix and the surface of the glass filler: 3-aminopropyl silane (Unisil U-13) was used as a coupling agent. The adhesion promoter was incorporated directly into the epoxy resin in an amount of 0.5% by weight of the filler according to producer data.

The prepared liquid compositions filled with waste filler were poured into the silicone molds with cavities for casting tiles with the following dimensions: length (110 mm), width (110 mm) thickness (4 mm). During cross-linking, the closed silicone mold was rotated by a rotator mixer for 24 h to obtain a homogeneous distribution of the filler in the matrix during curing and prevent it from settling. The rotational speed of the mold during crosslinking was 10 rpm. This speed is sufficient to prevent sedimentation and, at the same time, small enough to prevent the centrifugal movement of filler particles in the polymer matrix. From composite tiles bar samples for mechanical tests with dimensions 10 × 100 × 4 mm was cut. After cross-linking, the composites were seasoned in ambient conditions for 7 days.

3.4. Composite characteristic

Mechanical properties tests (flexural strength, impact strength) were carried out for epoxy composited filled with waste CRT glass. Strength properties of filled composites were determined under static bending according to PN-EN ISO 178 standard: Plastics – Determination of Flexural Properties. The flexural strength test (stress at the first fracture) was performed using the Instron TT-CM universal testing machine with a force measuring head with a range of up to 0–5 kN and an accuracy of 1 N. The test was carried out with the supports spacing of 64 mm and the test speed of 10 mm/min.

Impact strength test was performed according to the standard PN-EN ISO 179-1:2010: Determination of Impact Strength Using the Charpy Method – Part 1: Non-Instrumental Impact Test. Unnotched rectangular specimens with a cross-section of 4 × 10 mm placed on two supports were impact bent and the work required to break them was determined. In the test, the 1 J Charpy hammer (Wholgang Ohst) with the plane direction of impact was used.

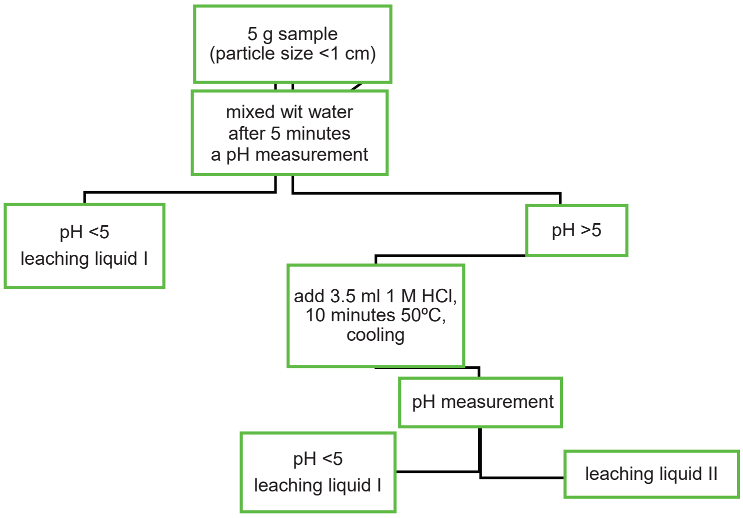

Fig. 2. Diagram of the leaching liquid selection for TCLP procedure
Source: own elaboration based on [22].

Rys. 2. Schemat doboru cieczy wymywającej do procedury TCLP
Źródło: opracowanie własne na podstawie [22].

3.5. Leaching tests

When using waste materials in new materials and products, the safety of their use is a concern. Due to its chemical composition and the content of toxic heavy metals, CRT glass is a difficult material to recycle. Heavy metals leaching out of waste or products made of it, in particular lead, may show mobility in the environment, leading to its contamination. Through the leachability tests, we assessed the metal immobilization by the polymer matrix of the composite and determined the leachability of metals from waste glass. The leachability of selected heavy metals was tested for both the glass filler (ground CRT glass) and the obtained composites.

As samples for the study of the leaching of metals from composites, composites samples after strength tests were used, which were shredded to the required grain size below 4 mm and further prepared according to appropriate test procedures, depending on the determination methodology used. The leaching test was performed according to the TCLP method (toxicity characteristic leaching procedure). This test procedure is a chemical analysis process used to determine whether there are hazardous elements present in the waste. The test involves a simulation of leaching through a landfill and can provide a rating that can prove if the waste is dangerous to the environment or not. The test samples used in this assay were ground to a granulation size below 4 mm and subjected to multi-stage selection. The waste glass samples weighing 5 g were preliminarily assessed by vigorously mixing with water in a beaker for 5 min and then pH evaluation. Depending on the pH of the preliminary test obtained (Fig. 2), two different types of eluting solutions were used for the tests. Leaching solution I for a pre-test pH below 5 cm^3 or 3.5 cm^3 of a 1 M hydrochloric acid (HCl) solution was added, the sample was stirred and heated to 50°C and kept at this temperature for 10 min.

After cooling, the pH was again measured and the eluting solution was selected based on the pH measurement obtained. For samples with a pH below 5, leaching solution I was used, while for samples with a pH above 5, leaching solution II was used in the

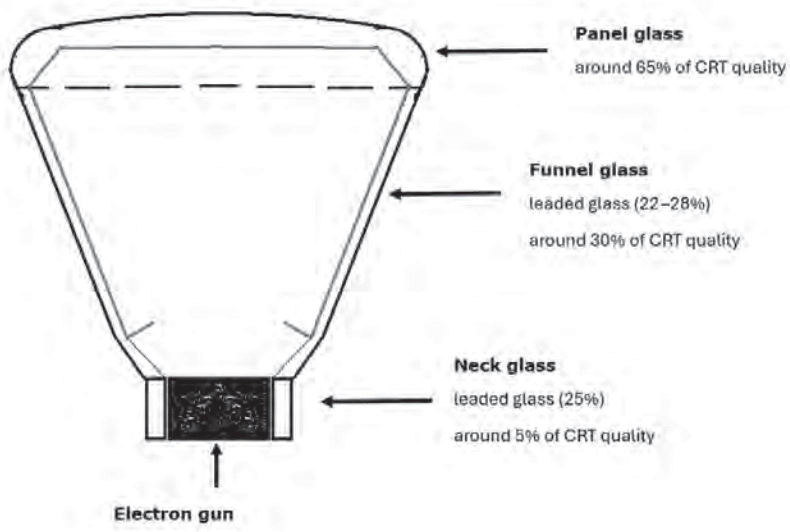

Fig. 3. Composition of CRT monitors
Source: [7, p. 955].

Rys. 3. Skład monitorów CRT
Źródło: [7, s. 955].

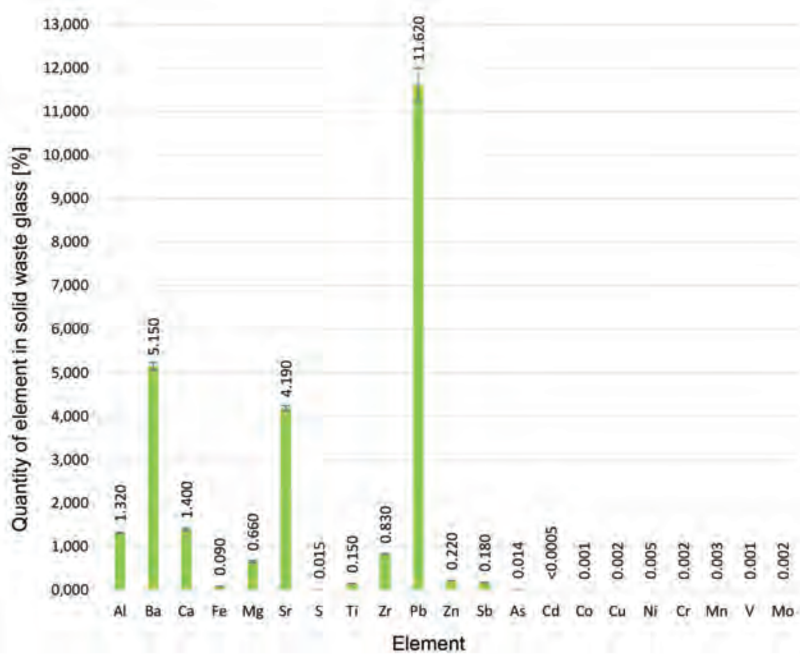

Fig. 4. Composition of CRT glass based on chemical analysis results

Rys. 4. Skład szkła CRT na podstawie wyników analiz chemicznych

Table 1. Physical properties of CRT glass fillers
Tabela 1. Właściwości fizyczne wypełniaczy ze szkła kineskopowego

Sample	Density [g/cm^3]	Bulk density	pH of water extract	Volatile matter at 105°C [%]
Unmodified CRT glass	2.79	0.64	8.14	0.68
Modified CRT glass	2.79	0.64	9.4	0.06

proper sample. The composition of the eluting solutions was as follows:

– Leaching solution I: 500 cm^3 of distilled water, 5.7 cm^3 of glacial acetic acid, 64.3 cm^3 of 1 M NaOH solution; the solution is diluted to 1000 cm^3 and the pH is measured, which should be 4.93 ±0.05.
– Leaching solution II: 5.7 cm^3 of glacial acetic acid is added to 500 cm^3 of distilled water and diluted to 1000 cm^3; the pH should be 2.88 ±0.05.

For tests according to the TCLP procedure, a sample weight of 100 g of waste was used.

The sample and the eluting solution were shaken by an RL-2002 rotator (JW Electronic) at room temperature for 18 h, then the obtained eluate was filtered through a borosilicate fibers filter, the pH of the filtrate was determined and acidified to pH <2. The obtained solution was subjected to qualitative and quantitative analysis for the content of selected metals such as: Ba, Ca, Pb, Cd, Zn, Sr, Na, Hg.

4. Results and discussion

4.1. CRT glass characteristic

A typical CRT glass may contain 13–35% lead oxide depending on the element of the picture tube from which it is derived (Fig. 3). The CRT screen glass is homogeneous barium strontium glass, while the funnel glass is lead glass. In the screen part, apart from barium oxide, responsible for protection against radiation, there are also oxides of silicon, sodium, potassium, aluminium in the funnel, lead oxide [7, 8, 10, 17].

The results of the research on the elemental composition of CRT glass used as a filler for polymer composites are shown in Fig. 4. The data presented in Fig. 4 illustrate the elemental composition analysis of waste CRT glass, where the elements are found in a chemically bound form as metal oxides. The data shown in the graph refer to the percentage content of these elements in the glass, with the highest amount being lead in the form of lead oxide. Elemental lead content was 11.62 ±0.376%. The tested CRT glass also contains 5 ±0.094% barium (Ba) and 4 ±0.049% strontium (Sr), aluminum (Al) and calcium (Ca) in amounts of 1.3 ±0.015% and 1.4 ±0.030%, respectively. The remaining elements tested are present in amounts below 1%. Cadmium, which is a highly toxic element, is present in an amount below <0.0005% (below the quantification limit of the apparatus). The composition of used glass was shown in Fig. 4.

The tested CRT glass, due to the content of heavy elements in the composition of the glass, has a higher real density than flat glass, the density of which is approx. 2.0 g/cm^3. The pH of the aqueous extract with glass is slightly basic, the application of aminosilane modification increases the alkalinity of the CRT glass (Table 1).

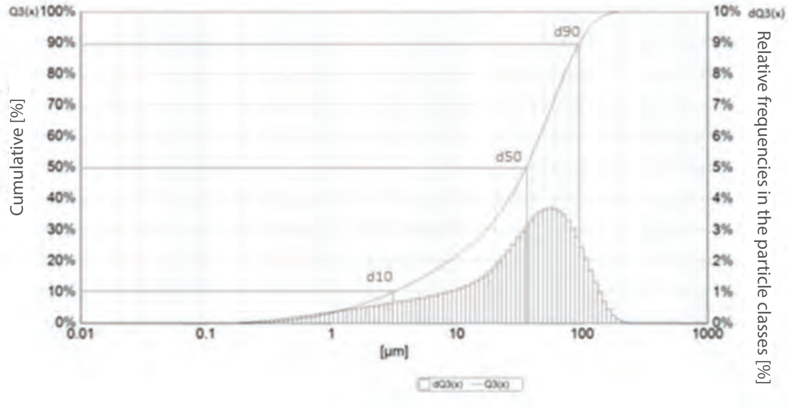

Fig. 5. Cumulative curve of the particle size distribution and particle size distribution curve of ground CRT glass

Rys. 5. Skumulowana krzywa rozkładu wielkości cząstek i krzywa rozkładu wielkości cząstek rozdrobnionego szkła kineskopowego

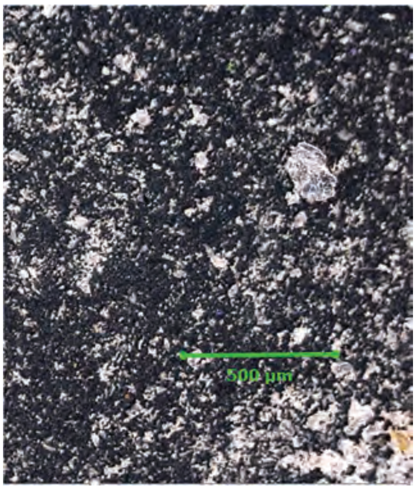

Fig. 6. Microscopic image of CRT glass (fraction <90 µm)

Rys. 6. Obraz mikroskopowy szkła kineskopowego (frakcja poniżej 90 µm)

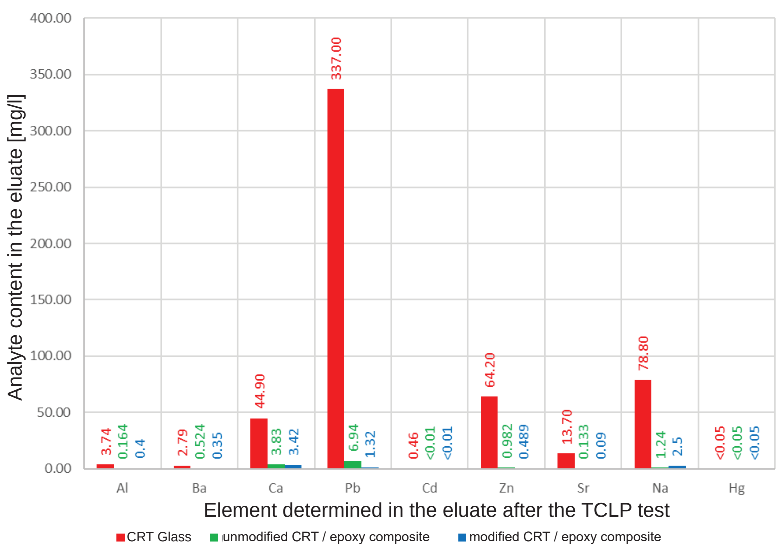

Fig. 7. Leaching of heavy metals from CRT glass and its epoxy composites

Rys. 7. Wymywalność metali ze szkła kineskopowego i jego kompozytów epoksydowych

By laser diffraction method cumulative curve of the particle size distribution of ground CRT glass was determined (Fig. 5). The characteristic parameters of the cumulative distribution d10, d50, d90 are respectively: 3.10 µm, 35.75 µm and 95.28 µm. The median diameter for CRT glass is 35.75 µm.

On microscopic image, it can be observed that the tested waste glasses are characterized by irregular particle shapes and non-uniform graining. CRT glass particle have sharp fracture edges (Fig. 6)

4.2. Leaching tests of composite

Fig. 7 shows the results of the leachability test for crushed CRT glass and its composites with epoxy resin (35 v/v% filler). For comparison, the leaching procedure was carried out taking into account the same amount of waste material (quantitatively in composites as for the filler) from which heavy metals were leached under the test conditions.

The washability of Al, Ba, Ca, Pb, Cd, Zn, Sr, Na is lower for epoxy composites both with and without the use of aminosilane modification. There was a significant decrease in lead leachability from 337 ±6.08 mg/l for CRT glass to 6.94 ±0.19 mg/l when using only epoxy matrix and to 1.32 ±0.05 mg/l when using a coupling agent (3-aminopropylsilane). The cadmium leaching was limited to below 0.01 mg/l (below the determination limit of the apparatus). Mercury is also eluted below 0.05 mg/ml (below the quantification limit of the apparatus).

In the case of Na, Ca, Al, there is an increase or a slight decrease in elution with the use of a coupling agent. This may be due to the nature of the glass matrix used as filler.

In the case of SiO_2, Fe_2O_3, Al_2O_3, hydrogen bonds are formed with water molecules upon contact with water. At the same time, the Na^+ and Ca^+ ions used as modifiers of the glass network are washed out in the water environment, leaving a poor porous surface. In an aqueous environment, the wettability of glass is reduced, leading to a decrease in the mechanical strength of polymer composites when exposed to water, this could lead to increase in leachability of heavy metals incorporated in CRT glass [21].

The addition of coupling agents should provide a strong chemical bond between the oxide groups on the surface of the glass and the resin particles constituting the polymer matrix, which translates into a possible improvement in mechanical properties and better long-term stability of the composite.

For glass fillers for example fiberglass in the presence of water, coupling agents (of the aminosilane type) are hydrolyzed to silanol molecules which compete with water molecules to form hydrogen bonds with the hydroxyl groups present on the glass surface. The first step of this process is preparing filler by priming. In the second step, the –R groups present in the aminosilane

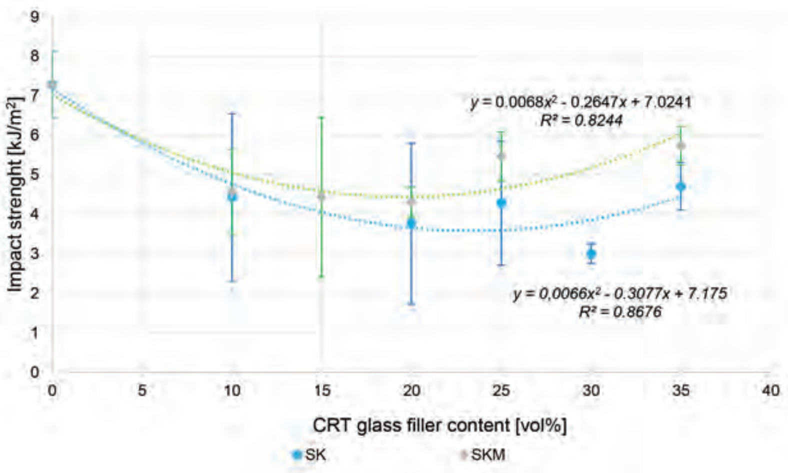

Fig. 8. Impact strength of epoxy composites containing unmodified (SK) and modified (SKM) CRT glass

Rys. 8. Udarność kompozytów epoksydowych zawierających niemodyfikowane (SK) i modyfikowane (SKM) szkło kineskopowe

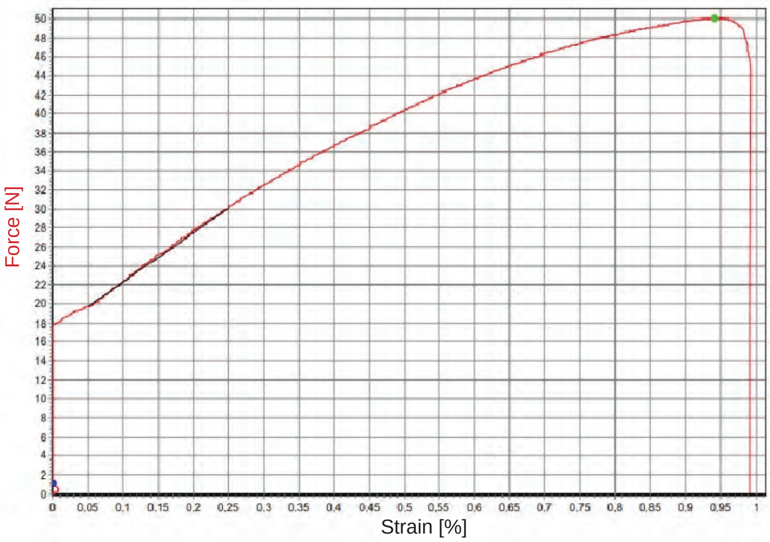

Fig. 9. Flexural strength graph of epoxy composite filled with 35 vol% of waste CRT glass filler (SK)

Rys. 9. Wykres wytrzymałości na zginanie kompozytu epoksydowego wypełnionego 35% objętościowymi odpadowego wypełniacza szklanego CRT (SK)

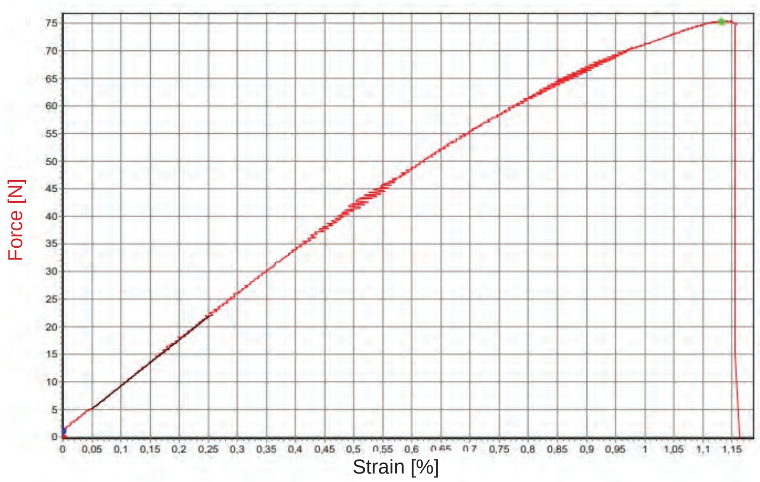

Fig. 10. Flexural strength graph of epoxy composite filled with 35 vol% of waste CRT glass filler with 3-aminepropylsilane modification (SKM)

Rys. 10. Wytrzymałość na zginanie kompozytu epoksydowego wypełnionego 35% objętościowymi odpadowego wypełniacza szklanego CRT z modyfikacją 3-aminopropylosilanem (SKM)

structure form bonds with the polymer structure during cross-linking of the epoxy resin, which results in a stronger bond and strength of the composite than when no coupling agent is used [21].

For the purposes of the research, the coupling agent was added directly to the resin containing component A, dispersed, and then the filler was added. During cross-linking, the silane particles introduced into the resin underwent grafting or copolymerization reactions with the resin. The results obtained after the TCLP leachability test suggest a positive effect on the reduction of leaching from the composite thanks to the use of such a modification method, especially in relation to Pb. This indicates the good effects of using CRT glass surface modification with amino silane used directly into the polymer matrix instead of using priming solution (which is used for pristine glass fillers) to reduce lead leaching into the environment.

4.3. Mechanical strength of composite

Waste ground CRT glass used as composite filler causes a decrease in the impact strength in relation to pure epoxy resin with aminosilane. It is generally observed effect of the powder fillers on the mechanical properties of polymeric materials (Fig. 8). Due to the uneven grain shape of the waste filler, the obtained results are characterized by a large scatter. The maximum impact strength value was recorded for the composition containing 35 vol% (corresponding to 55% by weight of the filler) containing aminosilane modified glass (marked as SKM in the graph) at 5.73 kJ/m^2. For the composite without the applied silane modifier (marked as SK), the highest impact strength was also observed at the content of 35 vol% CRT glass amounting to 4.7 kJ/m^2. The obtained impact strength values for epoxy composites filled with waste CRT glass as a filler are sufficiently high compared to casting resins and molding compounds according to DIN 16946-2 for type 1042-6, i.e. resins with 56–66% by weight of inorganic granular fillers for which is above 4 kJ/m^2 [23]. For comparison, it is worth to mention that the impact strength determined according to Saetchling for unfilled resins of this type should be >10 kJ/m^2, while the polymer matrix used for the tests is characterized by a lower impact strength at the level of 7.28 kJ/m^2.

On the basis of the above results, it can be concluded that the addition of a filler from waste CRT glass influences, with the appropriate selection of the composition of the composite, may have a positive effect on the preservation of impact strength. The use of an aminosilane bonding agent that undergoes a grafting reaction or copolymerization with the polymer matrix leads to the strengthening of the mechanical structure of the composite due to the creation of covalent bonds between the filler grains and the polymer matrix.

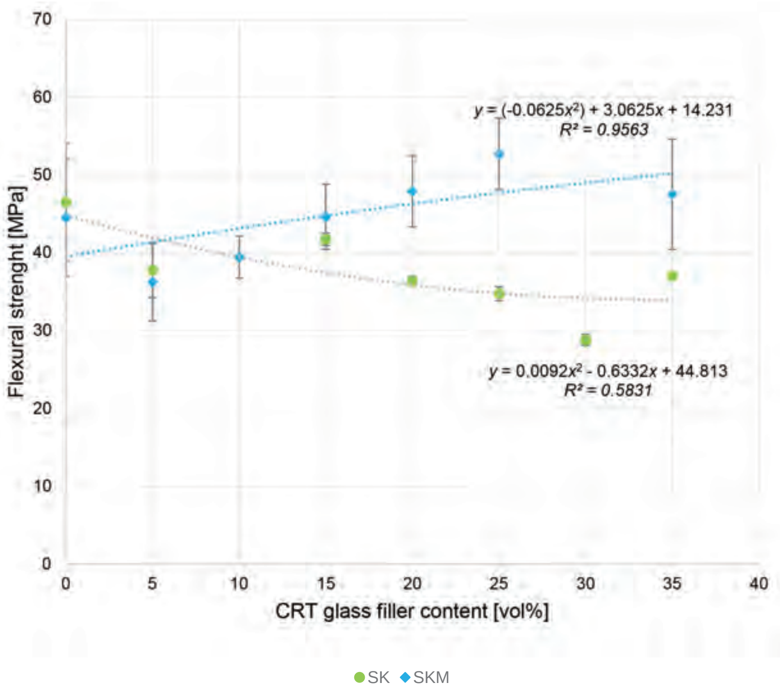

Fig. 11. Flexural strength of epoxy composites containing unmodified (SK) and modified (SKM) CRT glass

Rys. 11. Wytrzymałość na zginanie kompozytów epoksydowych zawierających niemodyfikowane (SK) i modyfikowane (SKM) szkło CRT

4.4. Flexural properties

During bending tests samples containing unmodified filler and modified with coupling agent break brittle (Fig. 9, 10). For composites filled with unmodified CRT glass (SK), a decrease in flexural strength is noticeable with an increase in the filler content. Epoxy composites with CRT glass and 3-aminopropyl silane (SKM) there is a noticeable increase in flexural strength with a filler content of 15% to 35% (Fig. 11).

The maximum flexural strength is achieved for a composite with a compactness of 25 vol% CRT glass and modification with a coupling agent that improves the adhesion between the filler material and the polymer matrix. The obtained values of flexural strength for epoxy composites filled with waste CRT glass as a filler are slightly lower than in the case of composite materials for use as old casting compounds classified according to DIN 16946-2 for type 1042-6, i.e. resins with 56–66% by weight of inorganic fillers, granular, for which the flexural strength should be at least 50 MPa [23]. For comparison, it is worth adding that the impact strength determined according to DIN 16946-2 for unfilled resins of this type should be >80 kJ/m^2, while the polymer matrix used for the tests is characterized by a lower flexural strength of 44–46 MPa. On the basis of the above results, it can be concluded that the addition of a filler derived from waste CRT glass causes a decrease by about 20–25% of the flexural strength of the composite containing unmodified CRT glass. The addition of CRT glass to the epoxy resin containing 0.5% of aminosilane increases the flexural strength of the composite by at least 6–7% in relation to the unfilled resin at the filler content of 20–35 vol%.

5. Conclusions

The conducted tests of composite materials with the use of waste material in the form of CRT glass as a filler for polymer composites confirmed the possibility of using such a filler in systems with a polymer epoxy matrix. The test results prove that the epoxy polymer matrix is able to provide both the appropriate strength parameters and the degree of immobilization of heavy metals allowing for the technical use of such material. A very large improvement in the waste neutralization capacity was observed as compared to the starting material (powdered waste). The effectiveness of the CRT glass immobilization process was noted in relation to lead, the leachability of which was reduced from over 300 mg/l to a level below the quantification threshold (<0.01 mg/l) with the use of aminosilane modification.

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CRediT authorship contribution statement

Katarzyna Suchoń: Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Visualization, Writing – original draft, Writing – review & editing.

Józef Stabik: Conceptualization, Formal analysis, Methodology, Supervision, Writing – review & editing.

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