Utilisation of bio-binder made of homogenised peat in crumb rubber-containing composites

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Abstract: The utilisation of the industrial residual products to create new value-added materials and to reduce footprint is a modern challenge of science and industry. Development of the new multifunctional and bio-based composites is an excellent opportunity for complex utilisation of industrial residual products. The study describes the preparation and characterisation of the three-phase bio-based composites. The main components are bio-based binder made of peat, devulcanised crumb rubber (DCR) from used tires and part of the fly ash the cenosphere (CS). Three-phase composite prepared in the form of a block for investigation of the mechanical properties and density and a form of granules for determination of the water and oil products sorption was investigated. This work investigated the dependence of the properties on the main component DCR and CS fraction. It was found, that maximum compression strength (in block form) observed for composition without CS and DCR addition - 79.3 MPa, the second highest value of compression strength is 11.2 MPa for composition with 27.3 wt% of CS. For compositions with bio binder content from 17.4 to 55.8 wt% and with DCR contents in range from 11.0 to 62.0 wt% compression strength is in range 1.1 to 2.0 MPa. Liquid sorption analysis (water and diesel) showed that the maximum saturation of liquids in both cases is set after 35 minutes and ranges from 1.05 to 1.4 g·g⁻¹ for water and 0.77 to 1.25 g·g⁻¹ for diesel. It was noted that 90% of the maximum saturation with diesel fuel comes after 10 minutes and for water after 35 minutes.

Keywords: crumb rubber, devulcanised crumb rubber, cenosphere, peat, homogenisation, biocomposite, hybrid material, bio-binder, oil absorption.

1. Introduction

Modern world suffering from many challenges such as generated waste increase, by plastic material pollution of nature and at the same time lacking the new efficient (lightweight, recyclable or decomposable, made of bio-sourced or recycled raw materials) materials. By this research, authors are introducing new biocomposite material made of two recycled materials – a cenosphere and devilisned crumb rubber and bio-sourced binder made of natural peat.

Cenosphere (CS) is low-density (0.25-0.55 g·cm⁻³)[1], inert, non-toxic, non-flammable powder-like material. With their hollow structure and lightweight properties have emerged as beneficial additives. These materials are derived from coal fly ash which is a significant polluter. Thus, application of cenospheres in composite materials design moves a concept of circular economy
forward. Cenospheres were chosen for specific properties such as low bulk density, high thermal resistance, good workability, and high strength [1]. Its addition to composite material helps make the material lightweight, improve impact absorption, and acoustic properties[2–5]. Here may also be some adverse effect on physical properties such as reduced compressive strength, increased porosity [2,6]. A decision on the trade-off between these different factors such as lightweight, compressive strength, cost-effective etc. is important in developing the material with desired properties.

Every year millions of tires are discarded, across the world, representing a severe threat to the ecology. By the year 2030, there would be up to 5000 million tires to be discarded regularly [7]. Discarded tires often lead to "black pollution" because they are nonbiodegradable and pose a potential threat to the environment [8] because tires have a long life and are nonbiodegradable. The traditional method of waste tires management have been stockpiling or illegally dumping or landfilling, all of which are a short-term solution. A growing amount of scrap tire waste has created a tremendous amount of waste being dumped which is not biodegradable. As Europe is taking the lead in recycling efforts, their use as fuel in the steel industry, cement industry, incineration facilities is being promoted [9]. Alternatively, they are also being used to create running tracks, playgrounds, artificial turfs, railways and in road building [10]. The utilisation of crumb rubber is also gaining traction by incorporating in concrete and rubberised asphalt [11]. This study proposes for the first time use of crumb rubber along with cenosphere, and natural binder peat in developing composite material. These solutions are in line with United Nations sustainable development goals by fostering conversion of waste material into value-added products.

A bio-composite is a category of bio-compatible and environmentally friendly composites that are bio-polyomers consisting of natural fibres. Bio-composites are composed of a wide range of organic and inorganic components such as natural and synthetic polymers, polysaccharides, proteins, sugars, ceramics, metal particles and hydrocarbon nanoparticles. Bio-composites come in a variety of forms such as films, membranes, coatings, fibres, and foams. There are several examples of using peat/sapropel binders, such as sapropel concrete, birch wood fiber and sanding dust, hemp shives, for composite materials [12,13]. These materials may be in the form of blocks or pellets. The obtained literature studies show the possibilities of using sapropel / peat as a raw material, were in the literature shown the possibilities to use them in the ecological construction were considered, which can be considered as promising materials for building materials and design products [14,15].

An extensive research has been done to improve mechanical properties and functionality of materials, as well as to develop environmentally friendly composite materials [16–18]. The use of bio-binders is of significant importance for the development of these bio-composites [19]. Bio-binders, also called bio-polyomers, are compounds derived from natural resources and are composed of monomer units that are covalently linked to form larger structures [20,21]. An example of a bio-binder is natural fibres. Natural binders differ in melt flow rate, impact properties, hardness, vapour permeability, coefficient of friction and decomposition. The water absorption of the bio-binder will also varies depending on the chemical composition of the processing conditions of the bio-binder [22]. The production of bio-based polymers using renewable materials has gained significant attention in recent decades in view of achievement the United Nation's Sustainable Development Goals. Latvia and Baltic region are extraordinarily rich with natural peat, one aim of the work is to investigate the possibility of a new application of natural peat – as bio-binder for hybrid composite material.

We are describing for the first-time the utilisation of devulcanised crumb rubber (DCR), homogenised peat (HP) and cenospheres (CS), for composite material development with bio-binder. This research is aimed to answer the question about the main component DCR-HP-CS content in the hybrid effect on composite material properties such as density, mechanical properties, absorption of the water, and oil products.
2. Materials and Methods

2.1. Raw materials and compositions

For designing a composite material in two form blocks and granule, a bio-binder made of HP, DCR and CS were used. Three general compositions with CS content 0.0, 5.0 and 10.0 wt% in a wet mixture were used. For each composition, the amount of DCR 0.0, 5.0, 10.0, 15.0, 20.0, 30.0 wt% were chosen. Samples designations and composition of the studied materials in block and granules are presented in Table 1 and Table 2. For the specimens, production used wt% of HP in wet condition (suspension with water content 85 wt%), but real DCR, CS and HP after drying also represented in Table 1 and Table 2 for an understanding of the entire composition of studied materials. For a better experience, all studied recopies represented from of ternary composition diagram Table 1.

Table 1 The composition of block and granules in a raw mixture (wet) and after drying, by wt% (part I).

| Designation of the composition | Wet mixture composition [wt%]* |
|-------------------------------|--------------------------------|
|                               | DCR | 0.0 | 5.0 | 10.0 | 15.0 | 20.0 | 30.0 | 0.0 | 5.0 | 10.0 | 15.0 | 20.0 | 30.0 |
|                               | HP  | 100 | 95.0| 90.0 | 85.0 | 80.0 | 70.0 | 95.0| 90.0| 85.0| 80.0| 75.0| 65.0 |
|                               | CS  | 0.0 | 0.0 | 0.0  | 0.0  | 0.0  | 0.0  | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0  |
|                               | Dried composite material formulation [wt%] |
|                               | DCR | 0.0 | 27.3| 44.2 | 55.8 | 64.1 | 75.4 | 0.0 | 22.1| 37.2| 48.1| 56.3| 68.0 |
|                               | HP  | 100 | 72.7| 55.8 | 44.2 | 35.9 | 24.6 | 72.7| 55.8| 44.2| 35.9| 29.6| 20.6 |
|                               | CS  | 0.0 | 0.0 | 0.0  | 0.0  | 0.0  | 27.3 | 22.1| 18.6| 16.0| 14.1| 11.3|

Table 2 The composition of block and granules in a raw mixture (wet) and after drying, by wt% (part II)

| Designation of the composition | Wet mixture composition [wt%]* |
|-------------------------------|--------------------------------|
|                               | DCR | 0.0 | 5.0 | 10.0 | 15.0 | 20.0 | 30.0 |
|                               | HP  | 90.0| 85.0| 80.0 | 75.0 | 70.0 | 60.0 |
|                               | CS  | 10.0| 10.0| 10.0 | 10.0 | 10.0 | 10.0 |
|                               | Dried composite material formulation [wt%] |
|                               | DCR | 0.0 | 18.6| 32.1 | 42.3 | 50.3 | 62.0 |
|                               | HP  | 55.8| 44.2| 35.9 | 29.6 | 24.6 | 17.4 |
|                               | CS  | 44.2| 37.2| 32.1 | 28.2 | 25.1 | 20.7 |
Figure 1. Ternary diagram of the dried composed material composition, by wt%.

To be used as a bio-based binder, natural peat (deposition Keizerpurvs, Cesis, Latvia) was preliminary processed hydrocavitation process. The raw peat (humidity 65-70%) was mixed with water and processed in high-speed multi-disc mixer-disperser (HSMD) with cavitation effect for obtaining the homogeneous water-peat slurry with dry matter contents 15±1 wt%. Raw peat agglomerates (a) before and treated peat particles (extracted from the suspension) after treatment by HSMD are shown in Figure 2.

Figure 2. Peat agglomerates (a) before and peat particles (b) after treatment by HSMD.

The rotation speed of HSMD used in experiments was 8500-9000 min⁻¹, and linear velocity of the working teeth was from 70 to 80 m·sec⁻¹. Therefore, the cavitation conditions required for slurry homogenisation were ensured. The technological scheme and HSMD common view is given in Figure 3. The treatment time by HSMD was 5 min, and 45 kg of the total amount of HP to ensure homogenous sludge-like HP.
The CS used in the experiments were supplied by Biothecha Ltd. (Riga, Latvia). Chemical composition is: SiO₂ - 53.8±0.5 %; Al₂O₃ - 40.7±0.7 %; Fe₂O₃ – 1.0±0.2 %; CaO – 1.4±0.2 %; MgO – 0.6±0.2 %; Na₂O – 0.5±0.1 %; K₂O 0.4±0.1 %. Loss of ignition is 1.1±0.1%. The grading composition is <63 µm – 1.70 wt%, 63-75µm – 3.86 wt%, 75-150 – 94.30 wt%. CS average wall thickness is from 7 to 15 µm. A detailed characterisation, including chemical analysis, particle size and morphology, has been published in [2,3,23]. The common appearance of the CS is represented in Figure 4.

DCR used for current research is produced using patented [24] mechano-chemical treatment technology at a semi-industrial pilot plant located in Riga (Latvia). A method comprises the processing of crumb rubber by grinding rolls at temperature 60-70 °C with the addition of devulcanisation chemicals. End-products represent a sponge-like aggregate of devulcanised crumb rubber. For the DCR milling-deagglomeration impact-type disintegrator DESI-15 (Desintegraator Tootmise OÜ, Estonia) at a rotation speed, 3000 min⁻¹ was used. The DCR was milled in direct mode five times (passes). For the present study, 0.25-2.0 mm fraction was used (Figure 5.) More details about CDR milling, particle size distribution and morphology is described by V. Lapkovskis et all. [25].
Figure 5. Digital optical micrographs of DCR 0.25-0.5 mm (a) and <0.25 mm (b) size.

For the production of the block, the components were manually mixed until the homogeneous mix, then placed into plastic moulds 140x180x20 mm. Samples were dried at room temperature for 20 days. After drying all specimens have been demoulded and left for ambient drying for ten days. To remove residual humidity, samples were dried at 105 °C for 48 h.

For the blocks granules, the components were manually mixed until the homogeneous mix, then placed rotary drum granulator with drum diameter 950 mm and rotation speed 80 s⁻¹. Samples were dried at room temperature for 2 days. In order to remove residual humidity, specimens were dried at 105 °C for 48 h. Standard production scheme of composite blocks and granules is demonstrated in Figure 6.

Figure 6. On the bio-based binder composite material in the shape of granules and block principal scheme.

2.2. Characterisation methods

2.2.1. Liquid adsorption

Determination of liquid (water and oil products) absorption was performed by immersing specimens in the liquid and checking the weight in a specific interval. The experiments were repeated five times for each composition/liquid, with a margin of error relative to the mean for each experiment. The liquid absorption ($W$) is calculated according to formula (1).

$$W = \frac{m_1 - m_0}{m_0}$$  \hspace{1cm} (1)

Where is:

$m_1$ – a mass of the sample saturated with liquid, g;
$m_0$ – dry mass (before immersion) of the sample, g;
$W$ – liquid absorption g/g.
2.3. **Used equipment and measurements devices**

High-speed multi-disc mixer-disperser with cavitation effect (HSMD) [26–28] for obtaining homogeneous water peat slurry with dry matter content 15±1 wt%. For the moisture content is determined using moisture analyser *Kern MRS 120-3*. Measurements are repeated 7 times using the standard deviation is determined standard error from the arithmetic mean. The Clatronic Multi Food Processor KM3350 (Clatronic GmbH, Kempen, Germany) with stainless steel container with a rubber-coated anchor-type mixer was used for wet mixture preparation at a rotation speed of 60 min⁻¹.

For specimens micro-optical inspection digital light microscope *Keyence VHX-1000* (*Keyence Corp. Osaka, Japan*) equipped with digital camera 54MPx and VH-112 Z20R/Z20W lens and scanning electron microscopy (SEM) – field emission *TESCAN Mira/LMU* and optical microscopy were used.

### 3. Results

#### 3.1. **Morphology of the obtained biocomposite block and granules**

The most characteristic difference of obtained bio-composites morphology in the form of block and granules is represented on Figure 7. The biggest difference in the appearance of the obtained composites is noted for block-shaped material with 0, 5 and 10 wt% of CS. The specimens containing 100 wt% of HP (composition 0–100–0) was strongly cracked after drying (Figure 7a), what is demonstrate high shrinkage, what is obviously, due to used HP without any additive contain 85 wt% of water. Detailed visual inspection of the parts of the cracked specimen, using magnification X50 times (Figure 7d) demonstrates a dense non-porous structure with white, crystal-like inclusions – sand particles. Analyzing them by applying of polarized light is concluded that this is mainly quartz particles and admixture of the limestone, which is a natural component of Baltic region peat. Addition of the 5 wt% of CS and/or 5 wt% of DCR strongly minimise shrinkage and cracking, the typical appearance of the 0–95–5, 5–95–0 or 5–95–5 specimens is demonstrated by (Figure 7d). But in comparison with highly-loaded composition 20–70–10, its geometry still differ from mould shape (Figure 7b, 7c). But is necessary to consider that real content of fillers – CS and DCR is much higher (Table 1, Table 2), because of water loss from HP is increased CS and CDR content in the composite. Specimens 0-95-5, 5-95-0 or 5-95-5 after drying has 0–72.7–27.3, 27.3–72.7–0 and 22.1–55.8–22.1 CDR–HP–CR mass ratio (or weight %) respectively. Effect of the shrinkage ratio decrease was noted by several works [2,29,30] mainly with a ceramic matrix material, where it is traditionally observed high shrinkage during the drying and firing [2,31].

In contrasts with block material, 0-100-0 granules have no significant morphological differences with other composition specimens - (Figure 7g-7j). In common, all made granules characterised by near-spherical shape and particle size distribution for all composition was: 1–2 mm - 7–15%, 2–6 mm - 10–20 and 6–10 mm - 60–70 wt%.
3.2. Mechanical properties and density of the obtained bio-composite block and granules

Obtained composites in from of blocks were tested for the compression strength and apparent density. The results are represented in a combined diagram in Figure 8. It is seen that exclusively high compression strength – 79 MPa corresponds to the pure peat-based bio-binder (0–100–0). Second highest compression strength – 11 MPa corresponds to the 0-100-5 composition with 5 wt% of CS in a raw wet mixture or 27.3 wt% in the composite material after drying (Table 1). Observation the parts of the cracked specimens 0-100-5 (with 27.3 wt% of CS) it has dense structure without cracks or voids the same as 0-100-0 (100 wt% of HP, Figure 7d) specimens. A significant difference in mechanical properties (79.3 and 11.1 MPa) could be explained by the presence of the filler with lower mechanical properties than quartz and limestone particles – CS. Introduction of the 27.3 wt% of the DCR leads to decreasing of compression strength to 7.6 MPa.

Increase of the CDR in composite in all of the studied cases lead to a significant decrease of compression strength, up to 1.5 ±0.4 MPa, but not less than 1.1 MPa (10-80-10 and 20-70-10).
Figure 8. Dependence of the apparent density and compressive strength of bio-composite I shape of a block on the DCR and CS fraction. The composition of DCR HP and CS fraction by indicated weight % in the wet mixture.

By applying the determined physical-mechanical properties data of the obtained samples to M. F. Ashby’s [32] compression strength and density summary diagram (Figure 9), it can be concluded that the obtained material is characterised by relatively low density and relatively high strength characteristic of bio-composites, which is one of the aims of this work. Pure bio-binder (0–100–0) composite material in coordinates MPa—kg·m⁻³ located in the upper zone of the polymer and elastomers area. Compositions 5–XX–X and 10–XX–X – with 5 and 10 wt% of DCR content in wet mixture coordinates MPa—kg·m⁻³ belongs to the lower zone of the natural material area.
Figure 9. Influence on the compliance of studied bio-composite (in form-factor of a block) with typical materials demonstrated in Ashby classification diagram (adapted from [32]).

3.3. Sorption of liquids in the structure of the granulated bio-composites

Obtained biocomposite granules were applied for sorption of water and oil products (diesel). Sorption kinetics were estimated for biocomposite by using diesel fuel as model-compound, as demonstrated in Figure 10 and Figure 11. All samples reach 90% sorbent water uptake capacity in 25-30 minutes but maximal saturation up to 35-45 min Figure 10. All series of the samples demonstrated near 1.0 g·g⁻¹ water sorption capacity saturation conditions. For the diesel 90% sorbent uptake capacity was noted in shorter time - in 5-10 minutes, but maximal saturation up to 35-45 min Figure 11. All series of the samples demonstrated from 1.0 to 1.5 g·g⁻¹ diesel sorption capacity at equilibrium conditions. Highest adsorption capacity is to 1.5 g·g⁻¹ for specimen 30–65–5, which corresponds to 68.0–20.6–11.3 ratio of components in a dry composite. It is necessary to admit that maximal saturation by liquids is for diesel, by except 30–70–0 maximal saturation was reached after 3-5 minute.

On the Figure 12 is demonstrated water and diesel uptake capacity, in g/g for granules is clearly seen that for most cases (by except 30–70–0, 5–90–5, 15–80–5 and 20–75–5) is greater sorption for water. For the composition series XX–XX–0 and XX–XX–10 water uptake significantly higher from 10 to 50%, but for XX–XX–5 series are nod showing big differences. However re-calculation sorption capacity from, mass ratio [g·g⁻¹] to sorbent mass to absorbed liquid volume [cm³·g⁻¹], taking in to account diesel density 0.85 g·cm⁻³, sorbent capacity for diesel will be higher for 15%.

Figure 10. Water adsorption, in g/g for granules compositions series with 0 wt% (a), 5 wt% (b) and 10wt% (c) of CS.
Figure 11. Diesel adsorption, in g/g for granules compositions series with 0 wt% (a), 5 wt% (b) and 10 wt% (c) of CS.

Figure 12. Sorbent water and diesel uptake capacity, in g/g for granules compositions

5. Conclusions

In current research three-phase composite material containing homogenised peat as bio-binder for water and oil products were produced in form of block and granules was produced for the first time. Obtained material in form of block cancerised by good combination of compression strength and density.

Obtained granulated sorbent containing 68.0–20.6–11.3 of CDR HP and CS has demonstrated up to 1.5 g·g⁻¹ maximal sorption capacity for diesel.

Composite material with CS content 27.3 wt% is characterised by highest value (by except the pure bio-binder) compression strength 11.2 MPa and at the same time apparent density 0.75 g·cm⁻³. HP as bio-binder and CS as lightweight filler could become a perspective material for lightweight bio-based structures design. Further investigations of the influence of CS content on the CS-HP bio-composite is foreseen.

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