



Article

Combined Carbon-Based Materials Modification of Polyamide Waste Agglomerate for Designing Sustainable Polymer Composites with Enhanced Performance

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Abstract

The topic of improving the strength and performance properties of secondary polyamide materials as part of their functional modification is a very relevant area of expanding the possibilities of secondary use of plastic waste. The article aims to conduct a systematic study of the combined modification of polyamide waste agglomerate by six different types of carbon materials to improve their technological and strength properties. PA6 waste agglomerate from polyamide clothing items, tights, socks, and various carbon materials were studied: masterbatch for polyamides MW-PA CB10, brown coal humic substances, coke residue from pyrolysis, a mixture of plastic waste, and finely dispersed coal enrichment waste. A sustainable polymer composite based on a modified agglomerate of PA6 waste was obtained by extruding pre-prepared raw materials in a single-screw extruder. The structural and morphological analysis of the studied carbon materials showed that, within the framework of the combined modification of polyamide-6 waste agglomerate, they should perform different functions related to their distinct morphology and chemical composition. Thus, humic substances can act as functional modifiers and compatibilizers due to their nanodispersity and a wide range of active chemical groups. In contrast, coke residue from pyrolysis and coal enrichment waste will act as a functional filler to improve the complex strength properties of sustainable polymer composites. As part of a study on the effect of modifying polyamide-6 waste agglomerate by carbon materials on its complex technological characteristics, it was demonstrated that humic substances enhance sustainable polymer composite's technological properties by increasing the melting temperature and melt flow index while reducing density. The increase in the functional effect of humic substances is due to the growth of a wide range of active chemical groups (hydroxyl, carboxyl, peptide). During the initial oxidation of brown coal, the coke residue from pyrolysis and coal enrichment waste served as a filler, increasing the sustainable polymer composite's density and melt flow index. As part of the study of the effect of



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modification by carbon materials on the complex strength characteristics of polyamide-6 waste agglomerate, it was shown that all carbon materials studied, except for coke residue, improve the strength characteristics of polyamide-6 waste agglomerate. The optimal content of different types of humic substances is 0.5% wt., while the sustainable polymer composite's impact strength and breaking stress during bending increase with the increase in the functionalization of humic substances during the oxidation of brown coal. It has been shown that the combination of small amounts of oxidized humic substances at the level of 0.5% by weight, as a functional additive with a masterbatch MW-PACB10 in an amount of 2–3.5%wt., provides materials with increased impact strength from 23 to ~48 kJ/m² and bending fracture stress from 115 to ~135 MPa, which allows returning secondary PA6 waste to the “traditional areas of primary PA6” in the manufacture of general technical parts and products.

Keywords: sustainable polymer composites; polyamide-6 waste agglomerate; carbon materials; combined modification; brown coal humic substances; pyrolysis coke residue; coal enrichment waste; strength characteristics

1. Introduction

Polyamide-6 (PA6), also known as nylon-6, is one of the most common engineering thermoplastics and is widely used in the production of technical parts, automotive components, textile fibers, films, and packaging materials due to its high mechanical and thermal properties, wear resistance, and chemical resistance. However, the production and use of large quantities of PA6 are accompanied by significant accumulation of industrial and household PA6 waste, particularly textile scraps, worn fishing nets, and automotive components, which require the development of technologies for their effective reuse and recycling.

The current development period in polymer materials science is characterized by increased scientific and commercial interest in composite polymer materials based on PA6 waste due to numerous opportunities for rapid, cost-effective expansion into specific applications [1–5]. Among the various PA6 blends, PA6 blends with polyolefins play the most crucial role [6,7]. These blends have several advantages over homopolymers. In particular, unlike polyolefins, they exhibit high resistance to petroleum products and abrasion. Compared to PA6, they exhibit lower water absorption, increased frost resistance, and improved impact resistance. Additionally, the use of polyolefin components alters the melt viscosity, enabling control over the technological properties of the mixtures, including their deformation and strength characteristics [2–5]. The modifying effect when compatible with PA6 is significantly enhanced by the functionalization of polyolefins through the binding of active functional groups to their macromolecules, which can form physicochemical interactions with PA6's functional groups and create strong bonds at the phase boundary [8]. Agglomeration is a promising technology for processing polyamide waste, which enables the restoration or even improvement of specific material properties. However, most agglomerates obtained from PA6 waste exhibit reduced properties compared to the primary polymer, including reduced strength, reduced molecular weight, increased hygroscopicity, and a heterogeneous morphology. This limits the scope of application of recycled material.

In this regard, it is essential to develop methods to modify agglomerates derived from PA6 waste to enhance their mechanical, thermal, and operational properties. Modern approaches include reinforcement with glass fibers, carbon fibers, the introduction of compatibilizers, the use of natural fillers, and the creation of bio-inspired structures. The

agglomeration of crushed PA6 waste is usually performed by extrusion, followed by pressing or granulation. It is important to note that the methods of modifying polyamide waste agglomerates by the melt method with the introduction of fillers–modifiers include a processing route in which the starting material (PA6 waste agglomerate) is necessarily dried to 0.12–0.20% wt. moisture before extrusion to minimize hydrolysis and “water” defects during melting. Further compounding is performed on a single-screw extruder at 210–230 °C and 70–95 rpm, after which the melt is formed into standard samples. It is in the molten state that modifiers/fillers with different functions are dosed, which ensures uniform distribution and controlled interaction with the PA6 matrix. However, after the first recycling cycle, a decrease in molecular weight and deterioration of viscoelastic properties are observed [8–10]. According to [8], after six cycles of PA6 agglomerate extrusion, a 25% decrease in ductility was observed, but the impact strength and modulus remained within acceptable limits for technical applications. Ergun et al. [9] found that when up to 15% of re-ground polyamide is included in a composition with primary PA6, it is possible to maintain a strength level above 80% of the original sample, primarily when additional drying or vacuum drying is performed before processing. Thus, PA6 waste in agglomeration can be utilized by incorporating fillers into composites, provided that moisture and morphology are controlled.

Another important method for enhancing the performance characteristics of agglomerates from PA waste is the incorporation of various reinforcing fibers. Modification of PA6 agglomerates with glass fibers is widely used in the automotive industry to manufacture technical parts. Research [10] has shown that modifying PA6 agglomerates with 30% glass fiber by mass restores strength to the level of primary PA6, exceeding 65 MPa, although elongation at break decreases by ~30%. Recent studies [11,12] have demonstrated the potential of using plant fibers (flax, hemp, and cellulose) as cost-effective, environmentally friendly alternatives to synthetic fibers for producing reinforced PA6 agglomerates. Introducing up to 20% natural fiber into the PA6 waste agglomerate increased Young’s modulus by +68%, while the density remained within the range of 1.25–1.30 g/cm³. To improve the performance characteristics of PA6 agglomerates, they are actively modified with fillers and modifying additives. Using mineral and organic fillers reduces the cost of PA6 agglomerate-based composites and improves specific characteristics, particularly stiffness and dimensional stability. Keskin et al. investigated the effect of adding 10–30% wt. of rice husks to PA6 cast agglomerates. With a rice husk content of 30% wt., the modulus of elasticity increased by 25%, although the tensile strength decreased slightly [13]. Liao et al. reported that adding 5% wood flour with LiCl reduces the melting temperature of PA6 sinter by 3.6–7.2 °C, contributing to better material processing at lower temperatures [14]. In general, organic fillers have a positive impact on the stiffness and processability of PA6 agglomerates but require control over particle size and moisture content.

Carbon materials are widely used to enhance the strength characteristics of various types of virgin primary and secondary polymer materials [15,16]. In the study by Hirçin et al., composites based on PA6 waste agglomerate with 10% wt. of short carbon fibers were obtained, in which the tensile strength increased by 21% and the elastic modulus by 32% compared to the unmodified agglomerate [17]. According to studies by Abdullah et al., nonwoven structures made of interwoven carbon fibers can achieve a uniform distribution of the reinforcing component within the PA6 agglomerate [18]. However, across all PA6 carbon fiber systems, there is a problem with phase compatibility: insufficient adhesion between the PA6 agglomerate and carbon fibers due to the loss of active end groups in recycled PA6 waste. One of the main problems when mixing PA6 waste agglomerates with other polymer or carbon components of different natures is the poor interphase adhesion. To improve it, compatibilizers are substances that reduce interphase tension. Yıldırım et al.

describe epoxy-containing polyhedral oligomeric silsesquioxane particles as compatibilizers in polyamide 6 (PA6) waste agglomerates modified with a thermoplastic elastomer. Such nanoadditives contributed to stabilizing the phase structure and increased impact strength by 30% after repeated processing [19]. The Ergun et al. study demonstrates the effectiveness of maleic anhydride-grafted polypropylene in the composition of PA6 waste agglomerates modified with secondary polypropylene and carbon fibers [9]. In general, the use of functional modifiers and compatibilizers to improve the properties of PA6 agglomerates is a critical factor in successfully integrating multicomponent PA6 agglomerate structures to enhance their operational, mechanical, and technological properties. The authors of this article investigated the promising co-modification of PA6 waste agglomerate using brown coal humic substances and carbon-containing masterbatch [20,21].

The effectiveness of combining PA6 waste agglomerate with carbon materials, in the form of humic substances, as a structural compatibilizer and masterbatch with a 10% wt. carbon content, as a coloring and reinforcing additive, was established. Within the framework of the model developed to predict the operational properties of the modified PA6 waste agglomerate, the dependence of the chemical composition on the complex of optimized technological and strength characteristics was determined. The developed modifications of the PA6 waste agglomerate are recommended for use in the same composition as traditional PA6 in primary areas of PA6 production, such as machine building and technical products. At the same time, the studies conducted do not reveal the mechanisms and factors underlying the effective combined modification of PA6 waste agglomerates with different types of carbon materials, which significantly limits the reproducibility of the recommendations for modifying a broader range of PA6 waste agglomerates with carbon materials. Combined modification using carbon-based fillers offers a promising approach to restoring and enhancing the properties of recycled PA6 waste agglomerates for the design of sustainable composites. This work emphasizes the role of humic substances and carbon masterbatch in improving interfacial adhesion, mechanical strength, and thermal stability of the design of sustainable composites for engineering and technical applications. This article aims to conduct a systematic study of the combined modification of PA6 waste agglomerates with various carbon modifiers and fillers.

The article aims to investigate the combined modification of polyamide waste agglomerates with carbon materials and fillers of varying nature to design sustainable polymer composites with enhanced performance.

2. Materials and Methods

2.1. Materials and Reagents

The materials of the research were:

- Agglomerate PA6 waste from polyamide clothing items, tights, socks, etc. (Material Wizard, Kharkiv, Ukraine). Such waste usually contains 70–95% by weight of PA6 matrix material, dyes, finishes, plasticizers, textile additives, elastane (up to 2–10% by weight), mineral and organic contaminants (dust, grease, surfactant residues, cosmetic residues), and remnants of sewing parts (polyester threads, labels). The agglomerate is obtained by melting the specified waste in a reactor with an anchor mixer and forming the molten mass into a lumpy material of irregular shape. Properties of agglomerate PA6 waste: density 1.132 g/sm³ and melt flow index (MFI) (230 °C, 2.16 kg/s) 0.25 g/10 min.
- Masterbatch for polyamides MW-PA CB10 (Material Wizard, Kharkiv, Ukraine). MW-PA CB10 made on the polyamide basis and intended for effective coloring of cast polyamides-6, -66, and compositions based on them without reducing the strength properties. MWPA CB10 composition and properties: carbon content —10% wt.,

density 1.132 g/sm^3 , and melt flow index (MFI) (230°C , 2.16 kg) 7.9 g/10 min . The polymer carrier provides excellent homogenization of pigment distribution in the dyed polymers and positively affects polyamide properties.

- Humic substances, which were obtained by extraction of brown coal from Moroziv deposit, Dnieper brown coal basin, Ukraine [16].
- Finely dispersed coal enrichment waste (filter cake) with a density of 1284 g/sm^3 .
- A carbon modifier in the form of coke residue from pyrolysis with a density of 1216 g/sm^3 . A mixture of plastic waste, consisting of polyethylene, polypropylene, polyethylene terephthalate, polyvinyl chloride, and polystyrene, in the form of films, trays, containers, and packaging, was studied. The prepared waste is pyrolyzed at 500°C in the absence of air.

2.2. Sample Preparation

A sustainable polymer composite based on a modified agglomerate of PA6 waste was obtained by extruding pre-prepared raw materials in a single-screw extruder, Sinban (RobotDigg Limited, Shanghai, China), at a temperature of $220\text{--}230^\circ\text{C}$ and a screw speed of $70\text{--}95 \text{ rpm}$ by filling a metal mold with molten material without specific chemical modification for samples in the geometric form of a rectangular parallelepiped with dimensions length $\times$ width $\times$ height of $15 \times 10 \times 5 \text{ mm}$ and cooling for 2 h at a temperature of 20°C with subsequent conditioning of the samples after removal from the molds at a temperature of 20°C for 1 day . Before obtaining and testing, unmodified and modified PA6 waste specimens were conditioned as follows to be either dry at $80\text{--}90^\circ\text{C}$ for 48 h using a dehumidifying dryer (dew point $\leq -30^\circ\text{C}$) to achieve $<0.12\text{--}0.2\%$ moisture, preventing hydrolysis and splay with test residual moisture by traditional oven drying for the weight to stabilize, and then storing at room temperature in a desiccator with silica gel. All unmodified and modified PA6 waste specimens were tested in a “dry-as-molded” state with a moisture content of $0.12\text{--}0.2\%$.

To determine the density, melt flow index, melting point, and strength characteristics and conduct microscopic, X-ray structural, and infrared spectroscopic studies, sustainable polymer composites based on modified PA6 waste agglomerate samples in the geometric form of a rectangular parallelepiped with dimensions length $\times$ width $\times$ height of $15 \times 10 \times 5 \text{ mm}$ were used, which were condensed at a temperature of 20°C for 1 day .

Humic substances were obtained using the classic chemical extraction method, which involves boiling the raw material in an alkaline solution. The raw material (brown coal) was ground to a particle size of $0.2\text{--}0.5 \text{ mm}$ and mixed with an aqueous solution of 1.5% sodium hydroxide (NaOH). It was kept for 2 days with periodic stirring. Then, humic substances were extracted in a stainless steel reactor at $55\text{--}60^\circ\text{C}$, with the solution stirred continuously for 60 min . After cooling, the alkaline humic substance solution was decanted, followed by centrifugation at 3000 rpm for 10 min to precipitate brown coal particles. The alkaline aqueous solution of humic substances was collected, and concentrated sulfuric acid was added dropwise until visible signs of coagulation of humic substances ($\text{pH} = 2$) appeared. Next, humic substances were separated by centrifugation and collected on a filter. The sediment was then washed with distilled water to a pH of $6.5\text{--}7.0$. After that, the humic substance sediment on the filter was dried at room temperature to a constant weight. The obtained oxidized samples of humic substances were first used to modify the PA6 waste agglomerate, which constitutes an important scientific and practical novelty of the modification methodology.

2.3. Characterization

The morphology and particle size of brown coal humic substances were characterized using dynamic light scattering (Zetasizer NanoZS, Malvern, Singapore), which was used to measure the size of nanoparticles in aqueous dispersions of colloidal polyelectrolyte brown coal humic substances.

The morphology of the carbon materials was characterized using HRSEM (High-Resolution Scanning Electron Microscopy) with a Zeiss Model V5.05 (Sigma, Kawasaki, Japan) at an accelerating voltage of 20 kV.

The morphology and particle size of humic substances and coke pyrolysis residue were characterized by the dynamic light scattering (DLC) method (Zetasizer NanoZS, Malvern) in aqueous dispersions of colloidal polyelectrolyte humic substances.

X-ray fluorescence microanalysis (XRF) with energy-dispersive X-ray spectroscopy (EDS) was performed using the Bruker XFlash 5010 system (Bruker BioSpin, Rheinstetten, Germany) to determine semi-quantitative elemental ratios and structural information. EDX quantification of light elements (e.g., C, O, N) in mixed organic–mineral matrices is severely hindered by low characteristic X-ray yields, high absorption within the sample, and spectral overlaps. Consequently, accurate measurement of these elements, particularly in, for instance, carbon-coated, non-conductive samples, requires careful correction for matrix effects and is generally less precise than for heavier elements.

Solid-state ^{13}C NMR spectra were recorded on Bruker Avance DRX 500 (Bruker BioSpin, Rheinstetten, Germany) and Agilent ProPulse 500 MHz spectrometers (Agilent Technologies, Santa Clara, CA, USA) at a resonance frequency of 101 MHz. Chemical shifts are given in δ scale (ppm).

Coke pyrolysis residue is characterized by chromatography on a Shimadzu chromatograph (Shimadzu Corporation, Kyoto, Japan) with a specialized multi-shot pyrolyzer Frontier Lab EGA/PY-3030D (Frontier Laboratories Ltd., Fukushima, Japan).

Microscopic studies were conducted using a Digital Microscope with a CMOS color sensor (Shenzhen Huahai Hong Communication Technology Co., Ltd., Changzhou, Jiangsu, China).

The study of impact strength and breaking stress during the bending of sustainable polymer composites based on a modified PA6 waste agglomerate was carried out on a pendulum head according to DIN 53435:2018-09 [22] at a temperature of 20 °C and a relative humidity 25%. The geometry of the test specimen for impact strength and bending breaking stress determination without notching was at its middle: 10 ± 0.2 mm width, 5 ± 0.2 mm thickness, and 15 ± 0.2 mm height. Tests for impact strength and breaking stress during bending were performed in accordance with DIN 53435 using a Dynstat device type Dys-e 9303 from Feinmechanik Kögel (Leipzig, Germany) under the following test orientation conditions: impact energy 11 J, speed of the pendulum at the moment of impact 3.5 m/s, pendulum angle 160° , stand between the axis of the pendulum and the center of impact 322 mm, pendulum moment 0.5155 Nm, and stand between the striking knife and the top surface of the clamp 22 mm. The number of replicates for each specimen was 10.

The density of the sustainable polymer composites based on a modified PA6 waste agglomerate is calculated in accordance with ISO 1183-1:2019(E) [23].

The melt flow index (MFI) study of sustainable polymer composites based on a modified PA6 waste agglomerate was conducted using the IIRT-M device at 230 °C and a load of 2.16 kg.

The melting temperature of the sustainable polymer composites based on a modified PA6 waste agglomerate was determined according to ISO 3146 [24] on a laboratory brass

disc with a diameter of 50 mm and a thickness of 19 mm, featuring a side hole for a thermometer with a diameter of 9 mm.

The obtained data were presented as mean $\pm$ standard deviation. Data normality was assessed for statistical analysis using Tukey's multiple comparison post hoc test within ANOVA, with sample size (n), standard deviation (SD), and p -values reported. The parameters used in the ANOVA analysis had a significance value of $p < 0.05$ at the 95–97% confidence level.

3. Results and Discussion

As carbon modifiers in the agglomerate of PA6 waste, dispersed materials in the form of humic substances of brown coal, coal enrichment waste, and coke residue from the pyrolysis of household polymer waste were studied. It is this variation in carbon modifiers that is associated with their similarity in dispersion and method of introduction into the polymer matrix; at the same time, these materials, by their nature, may have different chemical compositions and structural and morphological characteristics. As part of the technical and elemental analysis, the main characteristics of profitable brown coal and humic substances obtained from it were determined (Table 1). Samples of brown coal with varying degrees of oxidation were studied for a two-stage oxidation restoration process: initial unoxidized brown coal (BC1), brown coal oxidized for 10 h (BC2), and brown coal oxidized for 20 h (BC3). The oxidation process is accompanied by an increase in oxygen content from 24.52% to 34.19%, a decrease in carbon content from 69.55% to 58.60%, and a reduction in moisture content from 26.4% to 2.3%. Analyzing the data obtained in Table 2, it can be concluded that the studied samples of brown coal allow obtaining humic substances that have different quality indicators and the yield of these products is different: for the initial brown coal, 2.23% humic substances (HS1); for brown coal after 10 h of oxidation, 2.61% humic substances (HS2); and for brown coal after 20 h of oxidation, 4.94% humic substances (HS3).

Table 1. Results of technical and elemental analysis of brown coal samples.

Number	W	A ^d	S ^{daf}	V ^{daf}	C ^{daf}	H ^{daf}	N ^{daf}	O ^{daf} _d	Temperature of Oxidized, °C	Temperature of the Restored, °C
BC1	26.4	13.0	0.58	61.8	69.55	4.65	0.70	24.57	298.9	300.3
BC2	5.2	14.8	0.56	58.6	65.76	5.56	0.65	27.53	290.6	293.3
BC3	2.3	15.8	0.53	43.5	58.60	6.28	0.58	34.01	284.5	286.2

Table 2. Results of technical and elemental analysis of humic substance samples.

Number	W	A ^d	S ^{daf}	V ^{daf}	C ^{daf}	H ^{daf}	N ^{daf}	O ^{daf} _d	Temperature of Oxidized, °C	Temperature of the Restored, °C
HS1	9.7	51.2	0.40	73.3	59.09	6.31	0.87	32.91	282.3	302.8
HS2	12.5	33.1	0.49	56.4	61.61	5.60	0.53	31.53	273.6	274.4
HS3	16.4	33.1	0.54	59.3	61.64	5.99	0.55	31.02	275.4	283.8

In fact, oxidation of brown coal increases the yield of humic substances [25]. The results of experimental studies have shown that the study of humic substances from different types of brown coal allowed for the production of materials with similar characteristics in terms of oxygen content, O^{daf}_d (31.02–32.91%) and carbon C^{daf} (59.09–61.64%), and significantly different properties in terms of volatile and ash content. It is clear that the oxidation of brown coal significantly reduces the ash content, from 51.2% to 33.1%, and the volatile content (V^{daf}) from 73.3% to 56.4% of the humic substances obtained from it. X-ray

structural studies were conducted to establish the structural characteristics of different humic substances in brown coal [26] (Figure 1).

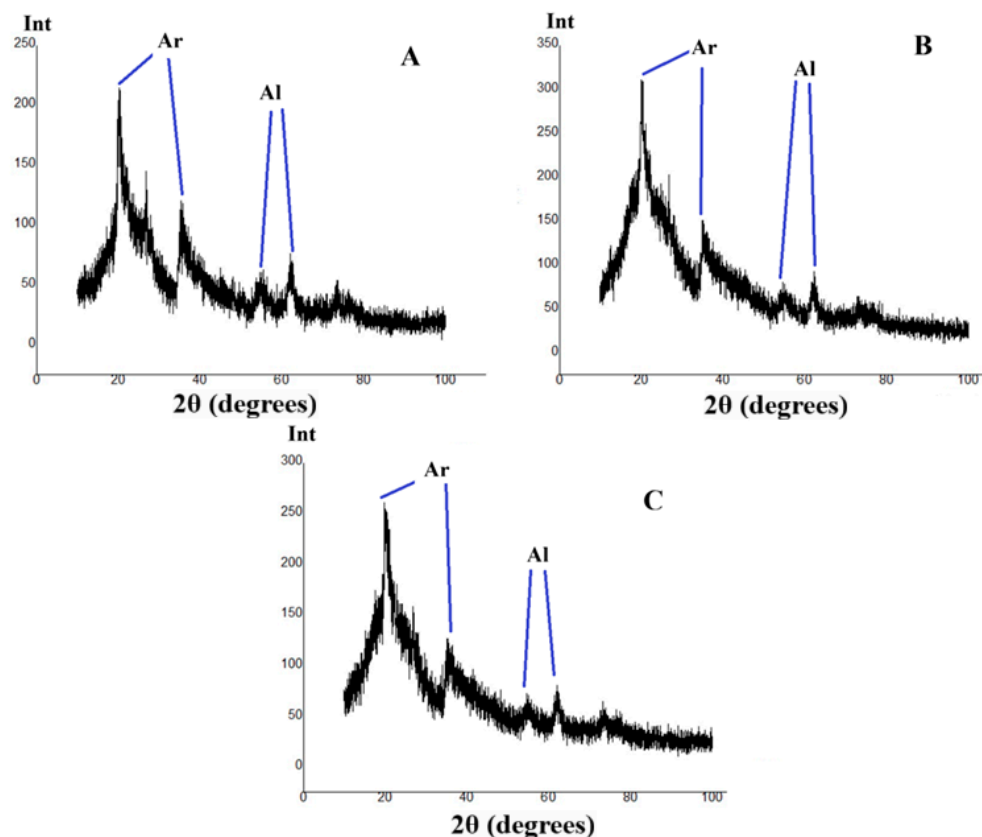


Figure 1. XRD curves: (A) HS1, (B) HS2, (C) HS3. Al—aliphatic carbon structures, Ar—aromatic carbon structures.

In the XRD profiles of the studied humic substance samples, pronounced peaks are observed at 27°, 38°, 55°, and 67°, corresponding to the crystal structures of humic substances. The first two peaks at 27° and 38° can be attributed to more condensed carbon structures in humic substances, which are primarily aromatic. In contrast, the 55° and 67° peaks are associated with aliphatic carbon in the structure of humic substances [27,28]. When studying the XRD profiles of different HR samples, it was found that in the series HS1 < HS2 < HS3, the number of aromatic structures in humic substances increases, associated with an increase in the degree of oxidation of brown coal. The latter correlates with the fact that the area of the aromatic peaks increases in the order HS3 > HS2 > HS1. At the same time, in the same series HS1 < HS2 < HS3, there is a decrease in the number of aliphatic structures, which indicates their transformation into aromatic structures as the degree of oxidation increases. The above characteristics of humic substances regarding changes in aromatic and aliphatic crystal structures during oxidation are well supported by solid-state NMR data (Figure 2). From the solid-state ¹³C NMR spectra of humic acids, one can clearly see the increasing proportion of aromatic carbon in the series HS1 < HS2 < HS3 with an increase in the intensity of its peaks at 120–150 ppm during the oxidation of humic acids, which is clearly visible from the increase in the peaks of oxygenated carbons at 50–90 ppm. The tendency to decrease in aliphatic structures of humic acids during oxidation is also confirmed, which corresponds to a gradual decrease in the intensity of signals (aliphatic carbon (alkyl, C–O) at 10–50 ppm.

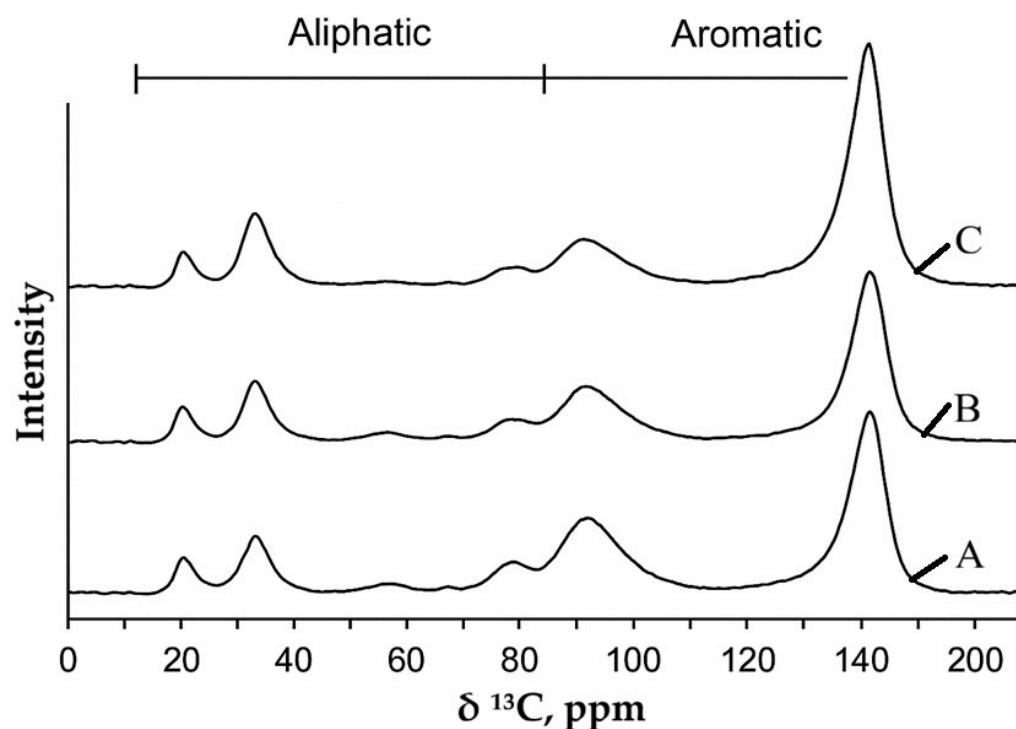


Figure 2. Solid-state ^{13}C NMR spectra: A—HS1, B—HS2, C—HS3.

Thus, it is concluded that with an increase in the degree of oxidation of brown coal, more crystalline aromatic structures are formed in its derivatives in the form of humic substances.

Figure 3 shows the results of the study of humic acids by IR spectroscopy.

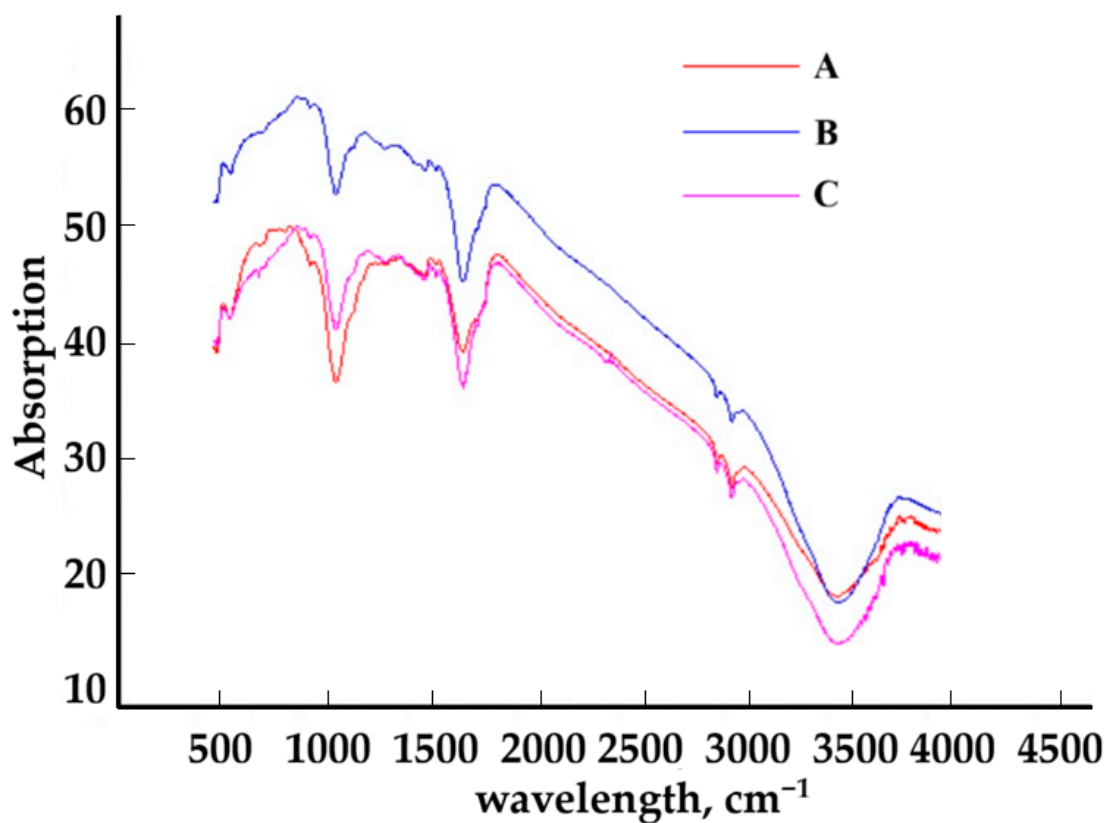


Figure 3. IR-spectra: A—HS1, B—HS2, C—HS3.

Analysis of humic acids with different degrees of oxidation shows that HS1 is characterized by clearly expressed peaks at about 3400 cm^{-1} , which indicate the presence of a large number of hydroxyl groups, at about 1720 cm^{-1} , which indicate a significant number of carboxyl and ketone groups in the region of $1000\text{--}1250\text{ cm}^{-1}$, which are associated with the presence of ester and phenolic groups. For HS2 humic acids, the most characteristic are clearly expressed peaks in the region of 1600 cm^{-1} , which indicate the growth of aromatic structures during the oxidation of humic acids; at the same time, there is a decrease in the intensity of the peak at about 3400 cm^{-1} , which indicates a reduction in the content of hydroxyl groups. For HS3 humic acids, an increase in the intensity of a clearly expressed peak in the region of 1600 cm^{-1} is observed, which indicates a further increase in the number of aromatic structures during the oxidation of humic acids; there is also the most intense peak near 1720 cm^{-1} , which indicates a high concentration of carboxyl groups. At the same time, there is a decrease in the intensity of the peak in the region of $1000\text{--}1250\text{ cm}^{-1}$, which indicates a reduction in C–O bonds. In fact, the results of IR spectroscopy of humic acids correlate well with the data of XRD analysis. In the series $\text{HS1} < \text{HS2} < \text{HS3}$, a decrease in the number of aliphatic structures in the composition of humic acids is observed, which indicates their transformation into aromatic structures with an increase in the degree of oxidation. It is important to note that the main functional groups of humic acids potentially have a specific effect on the polyamide matrix.

- Carboxyl groups are capable of forming hydrogen bonds and chemical bonds with amino groups of polyamides ($-\text{NH}_2$), which contribute to crosslinking or modification of the polymer matrix;
- Phenolic and hydroxyl groups can participate in hydrogen bonding, increasing hydrophilicity and adhesion;
- Carbonyl and methoxyl groups can affect the electron density and reactivity and can change the thermal stability of the polymer;
- Aromatic structures of humic acids have a significant effect on the properties of polyamide materials, especially in the context of their thermal stability, mechanical strength, and chemical activity.

The role of functional groups in humic acids is to modify the structure, properties, and functionality of polyamides, thereby increasing thermal stability and reducing the fragility of the polymer matrix. It is important to note that aromatic fragments of humic acids can provide the following properties of polyamide matrices:

- Thermal stability—due to the stability of aromatic rings;
- Structural rigidity—which can increase the elastic modulus of polymers;
- Rheological properties—the introduction of highly aromatic humic acids changes the viscosity of polyamide solutions and melts, which is essential for processing.

Figure 4 shows the results of microscopic studies of various samples of humic substances. Based on microscopic studies, it was found that all humic substances, regardless of their source (lignite), are characterized by the DLS method with polydisperse particle size ranging from 42 to 480 nm. The size distribution in the submicron range in solutions of all dispersed particles of all humic substances of brown coal is unimodal, broad, and, therefore, polydisperse based on the PDI value. The polydispersity index values range from 0.32 to 1.00 and depend both on the extraction conditions of all humic substances of brown coal and on their concentration (Figure 5).

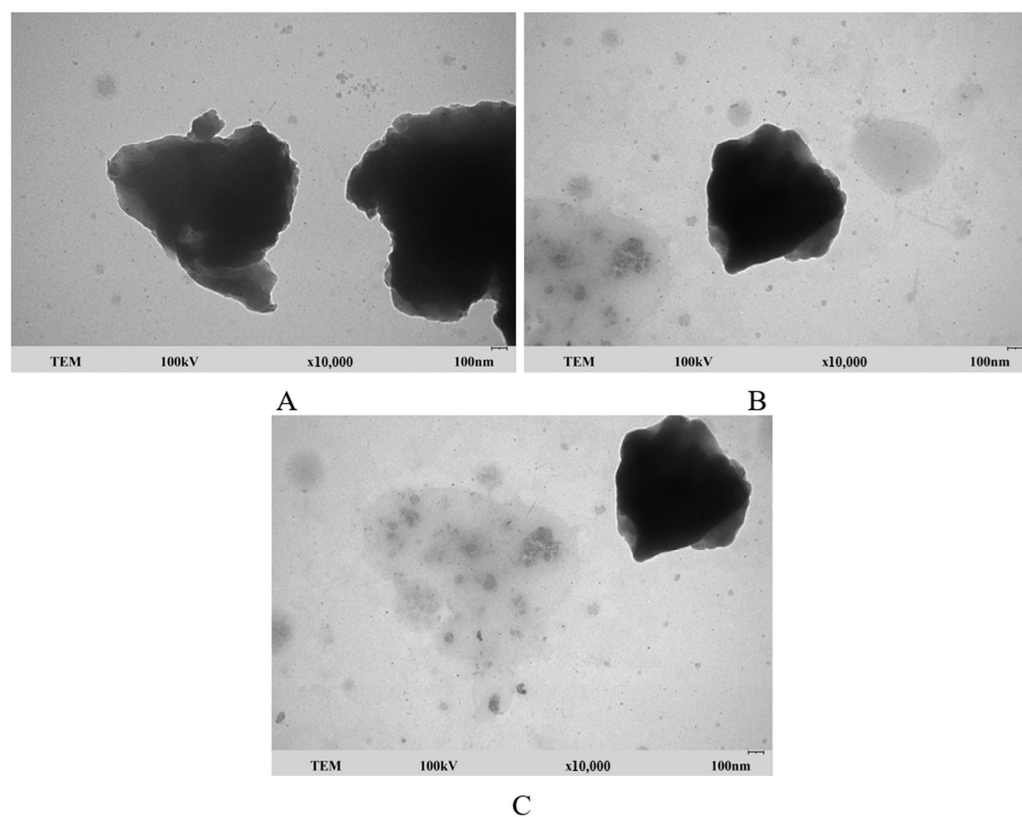


Figure 4. Microscopic studies of humic substances from different types of brown coal: (A) HS1, (B) HS2, (C) HS3.

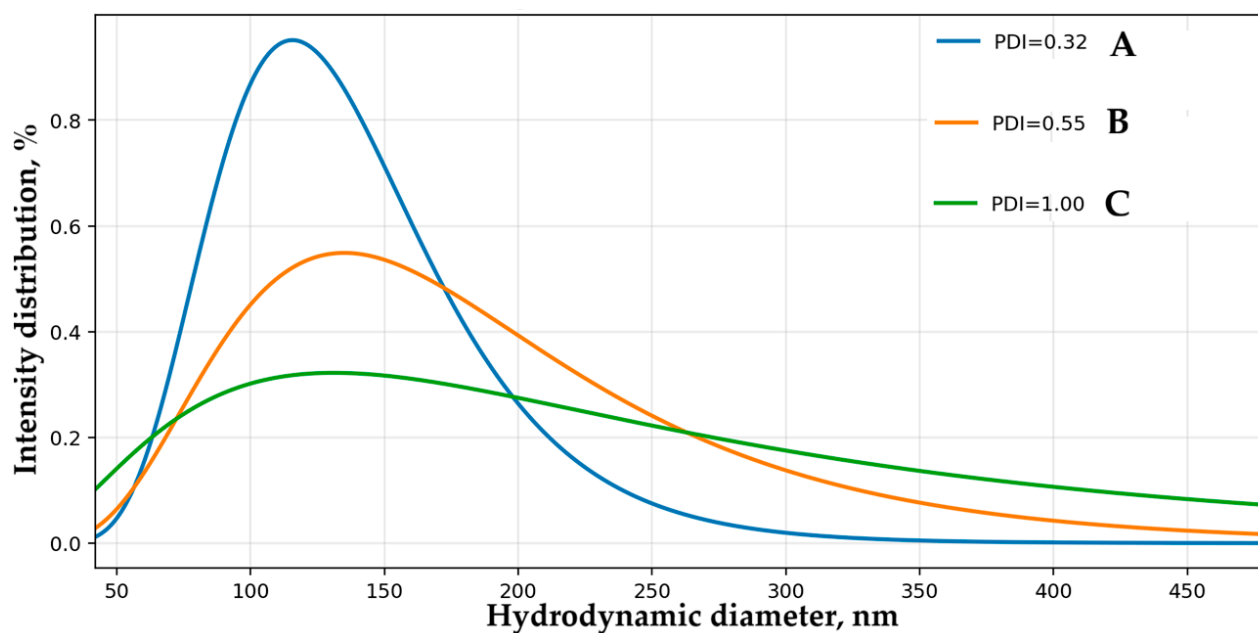


Figure 5. DLS intensity distribution plots of humic substances from different types of brown coal: A—HS1, B—HS2, C—HS3.

A structural and morphological analysis of coal enrichment waste was conducted. Figure 6 shows the results of the microscopic analysis.

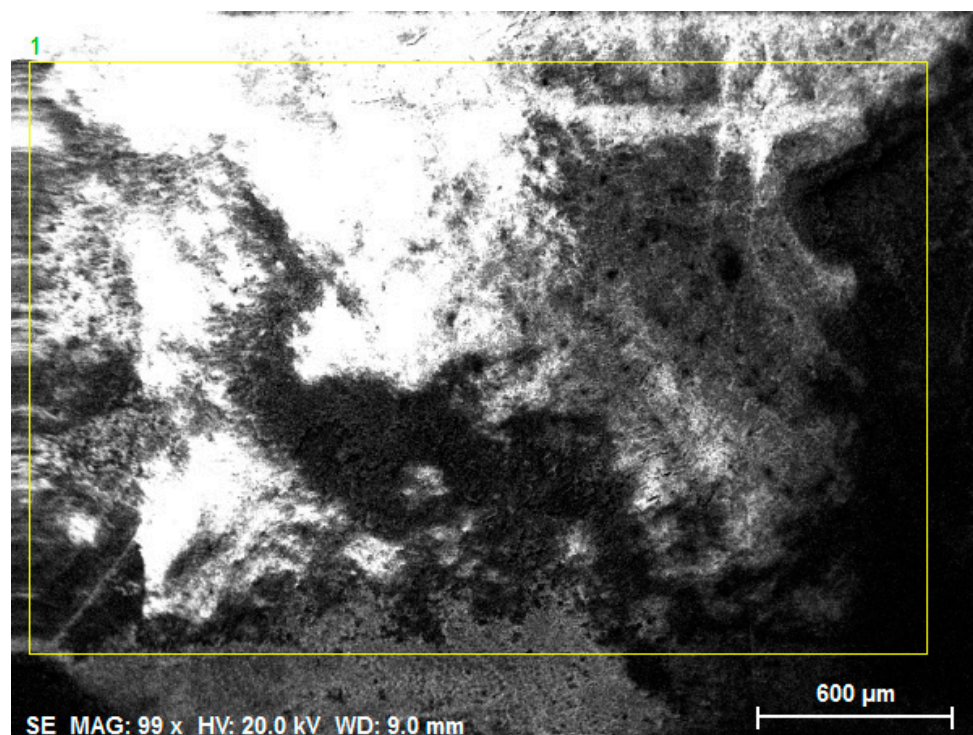


Figure 6. Microscopic studies of coal enrichment waste.

Coal enrichment waste is characterized by the DLS method with polydisperse particle size ranging from 25 to 180 nm with a polydispersity index of 0.9. It is important to note that the semi-quantitative elemental ratios of these wastes are dominated by oxygen (41.94% wt.), carbon (29.83% wt.), silica (12.99% wt.), and aluminum (8.52% wt.)—Figure 7.

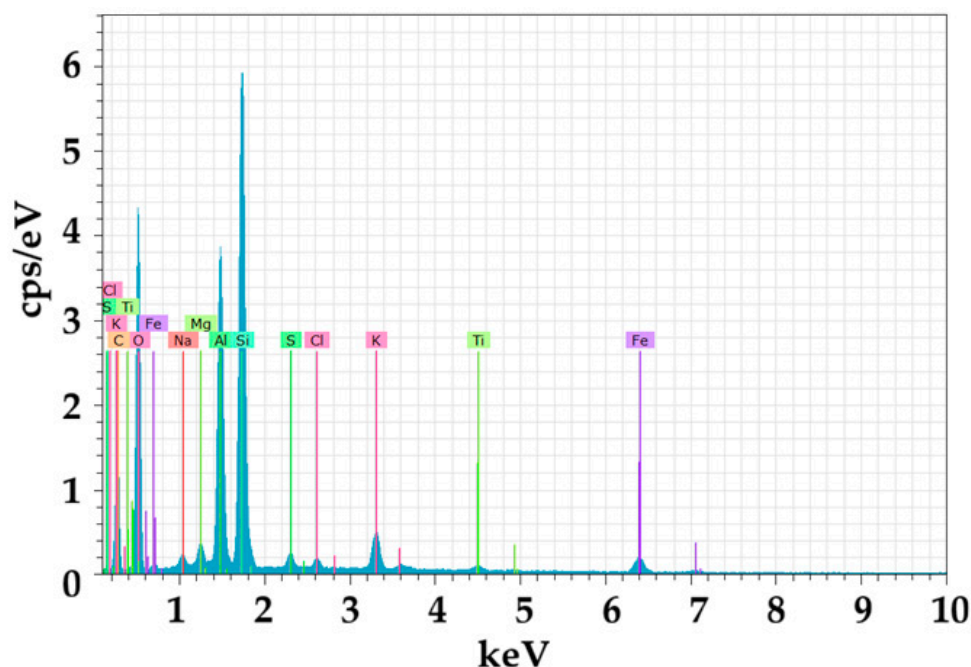


Figure 7. X-ray (EDX) spectrum of coal enrichment waste.

Significant amounts of silica and aluminum in coal enrichment waste are associated with the use of aluminosilicates [29].

A structural and morphological analysis of the coke residue from pyrolysis was performed. Figure 8 shows the results of the microscopic analysis.

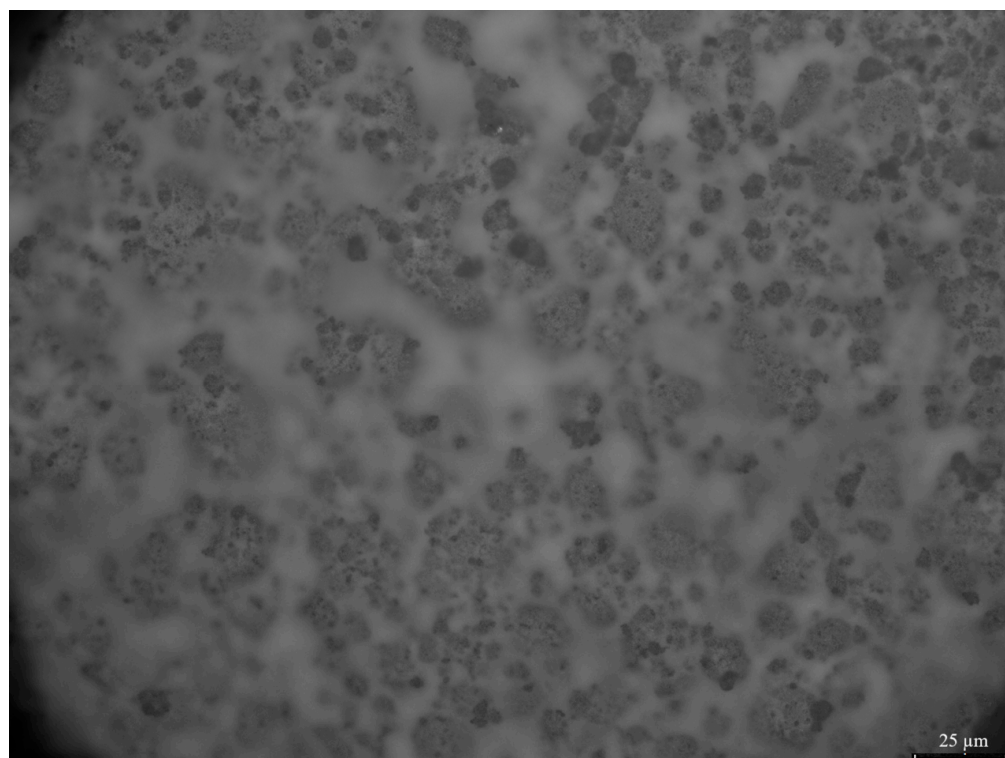


Figure 8. Microscopic studies of coke residue from pyrolysis.

Coke pyrolysis residue is characterized by the DLS method with polydisperse particle size ranging from 5 to 25 μm with a polydispersity index of 0.85. The results of chromatography analyses of liquid pyrolysis products show that all tested pyrolysis product samples contain monoolefin (54.3–56.7%), diolefin hydrocarbons (6.7–12.7%), and paraffins (31.6–38.7%)—Table 3.

Table 3. Explanation of the chromatographic analysis of liquid products of HPO pyrolysis by the main groups of substances.

Peak #	Area %	Height %	Name
1	2.35	3.12	1-Propene, 2-methyl-
2	18.29	27.60	Pentane
3	1.63	2.60	2-Butene, 2-methyl-
4	1.42	1.24	2-Methyl-1-butene
5	3.36	4.37	Pentane, 2-methyl-
6	16.94	21.81	1-Pentene, 2-methyl-
7	1.82	2.53	Hexane
8	2.21	2.84	Cyclopropane, 1,1,2-trimethyl-
9	0.82	0.90	Cyclopentane, methyl-
10	1.21	1.33	1,3-Pentadiene, 2-methyl-, (E)-
11	0.75	0.85	2,4-Hexadiene
12	1.82	2.10	1-Pentene, 2,4-dimethyl-
13	0.86	0.75	Cyclopentene, 1-methyl-
14	2.28	2.51	2,4-Dimethyl 1,4-pentadiene
15	3.83	3.43	Benzene
16	1.91	1.84	1-Heptene
17	1.61	1.53	Heptane
18	1.89	1.26	1,3-Pentadiene, 2,4-dimethyl-
19	2.91	1.88	Heptane, 4-methyl-
20	28.92	13.48	2,4-Dimethyl-1-heptene
21	2.04	0.96	Cyclohexane

This confirms that the destroyed polymer waste is derived from ethylene, i.e., its main component is polyethylene [30,31]. There may be several branches per thousand CH₂ groups in high- and low-pressure polyethylene. Diene and paraffin hydrocarbons were formed in the pyrolysis products due to thermodegradation processes.

In summarizing the structural and morphological analysis of the studied carbon materials, it is evident that they should serve different functions in further modifying the PA6 waste agglomerate, which is related to their distinct morphologies and chemical compositions.

Thus, humic substances can act as functional modifiers and compatibilizers due to their nanodispersity and a wide range of active chemical groups (hydroxyl, carboxyl, peptide, etc.) [32,33]. Due to the oxidation of brown coal and the formation of HS, the ash content decreases, their bonding ability decreases, and the role of the compatibilizer increases. In contrast, coke pyrolysis residue and coal enrichment waste will act as functional fillers to improve the strength properties of sustainable polymer composites.

As part of the study on modifying PA6 waste agglomerate with carbon materials, the effect of these materials on technological characteristics was first investigated—Table 4. The results in Table 4 confirm the distinct influence of the studied carbon materials on the PA6 waste agglomerate, which is associated with their unique morphology and chemical composition. Thus, humic substances enhance the technological properties of PA6 waste agglomerate by increasing the melting temperature and MFI while reducing the density. It should be noted that the functional effect of humic substances increases in the order HS1 < HS2 < HS3, which is due to the growth of a wide range of active chemical groups (hydroxyl, carboxyl, peptide, etc.) with an increase in the degree of brown coal oxidation [34,35]. In contrast, the coke residue from pyrolysis and the coal enrichment waste served as fillers, increasing the density and MFI [36,37]. It is important to note that, according to the principles of polymer physics, adding 25% solid particles always increases viscosity and lowers the MFI of polymer composites. In our case, the coke residue can act as a processing aid and lubricant due to the presence of graphite microplates, soot-like particles, π – π surfaces, and residual oils [38].

Table 4. Results of the effect of modifying the PA6 waste agglomerate with carbon materials on a set of their technological characteristics.

Type of Carbon Material	Density, g/m ³ ($n = 10, p < 0.05$)	Technical Characteristics	
		MFI, g/10 min ($n = 10, p < 0.04$)	Melt Temperature, °C ($n = 10, p < 0.05$)
HS1 content, % wt.			
0	1.132 ± 0.013	0.25 ± 0.013	230 ± 0.51
0.25	1.078 ± 0.012	0.67 ± 0.013	232 ± 0.49
0.5	1.072 ± 0.013	0.72 ± 0.014	235 ± 0.52
0.75	1.061 ± 0.014	0.73 ± 0.012	234 ± 0.50
HS2 content, % wt.			
0.25	1.152 ± 0.01	0.80 ± 0.01	234 ± 0.5
0.5	1.112 ± 0.01	0.83 ± 0.01	238 ± 0.5
0.75	1.101 ± 0.01	0.84 ± 0.01	235 ± 0.5
HS3 content, % wt.			
0.25	1.072 ± 0.011	0.84 ± 0.012	235 ± 0.51
0.5	1.051 ± 0.012	0.88 ± 0.013	240 ± 0.52
0.75	1.031 ± 0.011	0.90 ± 0.012	237 ± 0.39

Table 4. Cont.

Type of Carbon Material	Density, g/m ³ (<i>n</i> = 10, <i>p</i> < 0.05)	Technical Characteristics MFI, g/10 min (<i>n</i> = 10, <i>p</i> < 0.04)	Melt Temperature, °C (<i>n</i> = 10, <i>p</i> < 0.05)
Coke residue content, % wt.			
15.0	1.137 ± 0.011	0.29 ± 0.012	231 ± 0.51
20.0	1.143 ± 0.012	0.30 ± 0.013	233 ± 0.52
25.0	1.153 ± 0.013	0.34 ± 0.011	232 ± 0.49
Content of coal enrichment waste, % wt.			
15.0	1.158 ± 0.012	0.26 ± 0.011	225 ± 0.51
20.0	1.163 ± 0.011	0.29 ± 0.012	223 ± 0.50
25.0	1.171 ± 0.011	0.27 ± 0.011	220 ± 0.51

They can create boundary lubrication, reducing friction between polymer chains and between the polymer and the die walls. The distribution of carbon materials during the modification of the PA6 waste agglomerate is clearly shown in the microscopic studies in Figure 9.

Figure 9 clearly shows that all the humic substances studied were completely homogeneously distributed throughout the mass of the PA6 waste agglomerate; they are not visible on the surface of the samples, indicating their functional role as a structural modifiers and compatibilizers. Also, according to IR spectroscopy, it was found that with an increase in the content of humic substances in the PA6 waste agglomerate, changes are observed in the enhancement of the $\sim 3300\text{ cm}^{-1}$ (N–H $\cdots$ O, H-bonding) band, typical for the enhancement of hydrogen bonds and interphase interactions, which in PA6 corresponds to the stretching vibrations of the N–H of the amide group. Also, when HS, rich in phenolic and carboxyl groups, is introduced, intermolecular hydrogen bonds are formed in the HS-PA6 system, which is manifested in an increase in the intensity of the $\sim 3300\text{ cm}^{-1}$ peak, a shift of its maximum towards lower frequencies (red shift) and a broadening of the band—a characteristic sign of the enhancement or multiplicity of H-bonds. Also important are the changes in the region of the amide groups Amide I ($\sim 1630\text{--}1650\text{ cm}^{-1}$) and Amide I (C=O), sensitive to intermolecular interactions. With an increase in the HS content in the series HS1 < HS2 < HS3, the peak shifts to the lower frequency region near 10 cm^{-1} , which indicates a stronger interaction of C=O with the donors of H-bonds of humic groups, and its intensity increases. For the Amide II band ($\sim 1530\text{--}1550\text{ cm}^{-1}$), which includes N–H bending and C–N stretching vibrations, this peak is strengthened and shifts to the lower frequency region near 10 cm^{-1} , which corresponds to an increase in the number of N–H $\cdots$ O–HS hydrogen bonds and the formation of more stable PA6–HS complexes. At the same time, coke pyrolysis residue and coal enrichment waste are visually visible on the surface of the modified PA6 waste agglomerate samples, indicating their role as a functional filler for improving the complex strength properties. Further studies aimed to confirm the different functional effects of the studied carbon materials on modifying PA6 waste agglomerates when studying their strength properties—Table 5. The results in Table 5 show that all carbon materials studied, except for coke residue, improve the strength characteristics of sustainable polymer composites based on PA6 waste sinter. In our opinion, the lack of a positive modification result specifically for the coke residue of the PA6 waste agglomerate is due to its insufficiently functionalized composition and the absence of active centers, such as acid groups and branched aromatic fragments that facilitate π – π stacking. Noting the features of the interfacial interaction between the PA6 matrix and carbon fillers, it is important to note that coke residue from pyrolysis and coal enrichment waste is charac-

terized by a smooth and virtually functionally inert surface, which has low wettability and weak chemical activity [39], which leads to poor adhesion with the PA6 polymer matrix and increased melt viscosity of the mixture while complicating the impregnation of coke residue from pyrolysis and coal enrichment waste particles and cavities and dry zones in the composite mass. Insufficient adhesion without surface modification of coke residue from pyrolysis and coal enrichment waste leads to low strength characteristics of sustainable polymer composite with them and limits their use in structural parts. At the same time, the high functionalization of the humic substances surface due to the presence of carboxyl, hydroxyl, and other polar groups significantly increases the interfacial interaction energy, wettability, and chemical activity of the ability to form hydrogen bonds and ionic complexes with amide groups of PA6, which increases the hydrophilicity of the polymer surface and increases the strength of the interfacial interaction in the PA6–humic substances system [40,41]. This, in turn, allows us to significantly increase the complex strength characteristics of such composites. The optimal content of different types of humic substances is 0.5% wt., while the impact strength and breaking stress during bending increase in the order HS1 < HS2 < HS3, which is associated with an increase in the functionalization of humic substances during the oxidation of brown coal.

Table 5. Results of the study of the effect of the modification of the PA6 waste agglomerates with carbon materials on the sustainable polymer composite’s strength properties.

Type of Carbon Material	Strength Characteristics	
	Impact Strength, kJ/m ² (<i>n</i> = 10, <i>p</i> < 0.05)	Breaking Stress During Bending, MPa (<i>n</i> = 10, <i>p</i> < 0.04)
HS1 content, % wt.		
0	23 ± 0.51	115 ± 0.50
0.25	24 ± 0.49	115 ± 0.50
0.5	26 ± 0.50	117 ± 0.52
0.75	25 ± 0.51	122 ± 0.51
HS2 content, % wt.		
0.25	27 ± 0.50	120 ± 0.51
0.5	29 ± 0.51	125 ± 0.49
0.75	28 ± 0.49	122 ± 0.52
HS3 content, % wt.		
0.25	36 ± 0.51	130 ± 0.50
0.5	39 ± 0.50	135 ± 0.50
0.75	37 ± 0.49	132 ± 0.51
Coke residue content, % wt.		
15.0	25 ± 0.50	120 ± 0.51
20.0	26 ± 0.51	105 ± 0.52
25.0	27 ± 0.49	100 ± 0.51
Content of coal enrichment waste, % wt.		
15.0	23 ± 0.51	115 ± 0.52
20.0	26 ± 0.50	120 ± 0.50
25.0	29 ± 0.49	125 ± 0.51

Furthermore, the system’s PA6 waste agglomerate HA-MW-PA CB10 masterbatch was studied at an optimal HS3 content of 0.5% wt. The variable content of MW-PA CB10 masterbatch was 2–5% wt. (Figure 9). The combined modification of sustainable polymer composites based on the PA6 waste agglomerate with humic substances at a 0.5% wt. concentration in the MW-PA CB10 carbon masterbatch with a content of 2–3.5% wt. significantly improves most of the sustainable polymer composite’s strength properties—Figure 10. Under the achieved level of strength characteristics, these combined modified PA6 waste agglomerate

composites are superior to the previously obtained by the authors of the article of the PA6 waste agglomerate with 2% wt. of masterbatch MW-PA CB10 and 0.5% wt. of unoxidized humic acids of brown coal [20]. The impact strength increased from 43.5 kJ/m² to 48.1 kJ/m², and the breaking stress during bending increased from 126.4 MPa to 134.2 MPa. This pattern is associated with increased functionality of oxidized humic substances. The presence of a larger number of hydroxyl, carboxyl, peptide, and other oxygen-containing groups leads to an increase in the chemical binding force between the PA6 waste agglomerate and the carbon matrix of humic acid.

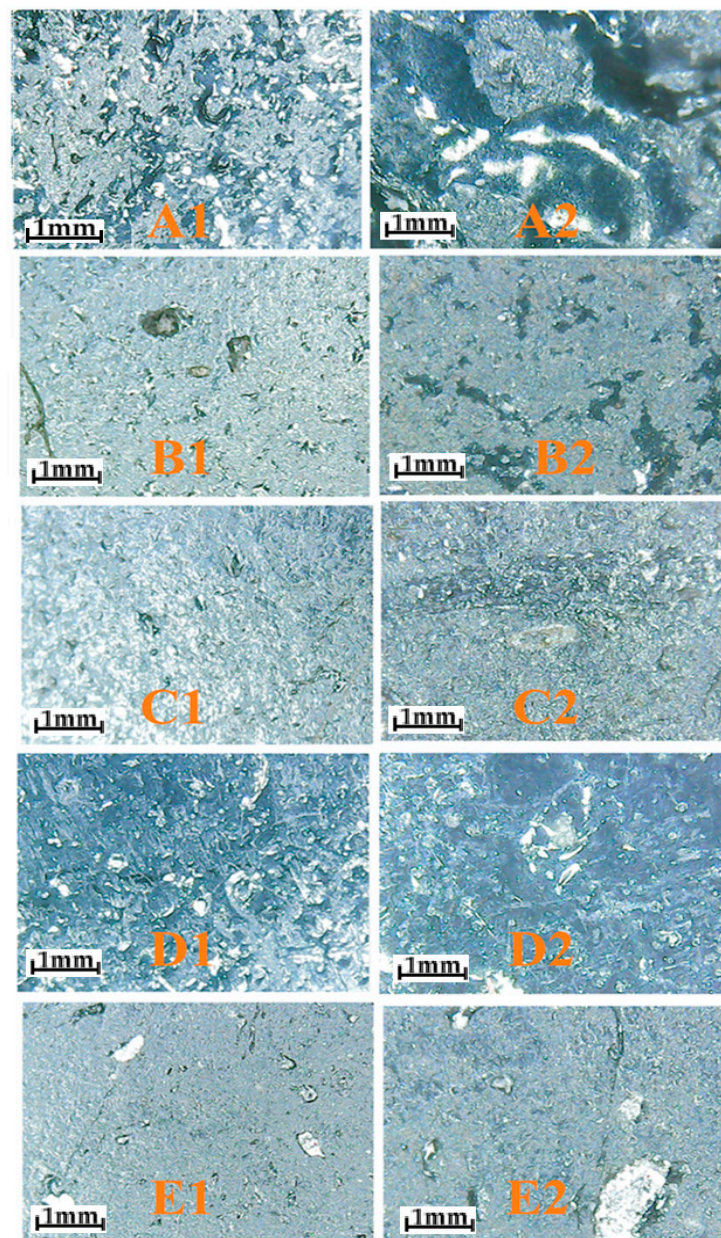


Figure 9. Microscopic photographs of the distribution of carbon materials during the modification of the PA6 waste agglomerate: (A1,A2) HS1 with magnifications of 100 and 500, respectively; (B1,B2) HS2 with magnifications of 100 and 500, respectively; (C1,C2) HS3 with magnifications of 100 and 500, respectively; (D1,D2) coke residue with magnifications of 100 and 500, respectively; (E1,E2) carbon enrichment waste with magnifications of 100 and 500, respectively.

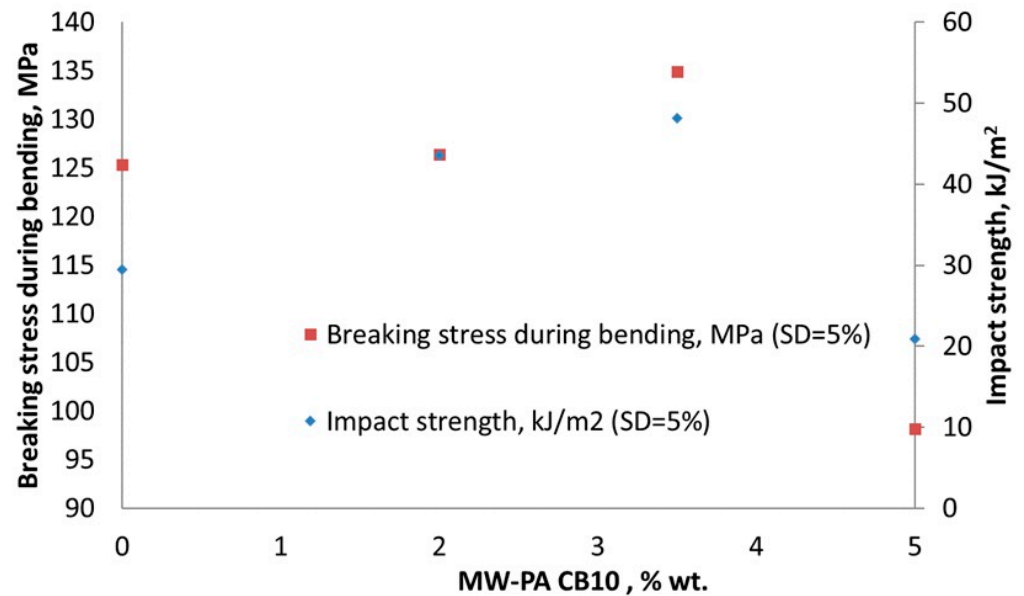


Figure 10. The MW-PA CB10 introduction impact on the PA6 waste agglomerate—HS3 0.5% wt. The system impacts strength and breaks stress during bending ($n = 10$, $p < 0.05$).

The latter aligns well with studies on the chemical binding force between PA6 and carbon, which established that understanding the chemistry of the carbon surface allows you to control the processes of forming effective composites [41–43]. With a further increase in the MW-PA CB10 content, a decrease in impact strength and bending stress is observed. This trend is associated with the maximum level of crystallinity, specifically for the modifier of sustainable polymer composites based on the PA6 waste agglomerate with humic substances at 0.5% wt. in the MW-PA CB10 carbon masterbatch content of 2–3.5% wt., which is clearly visible in Figure 11.

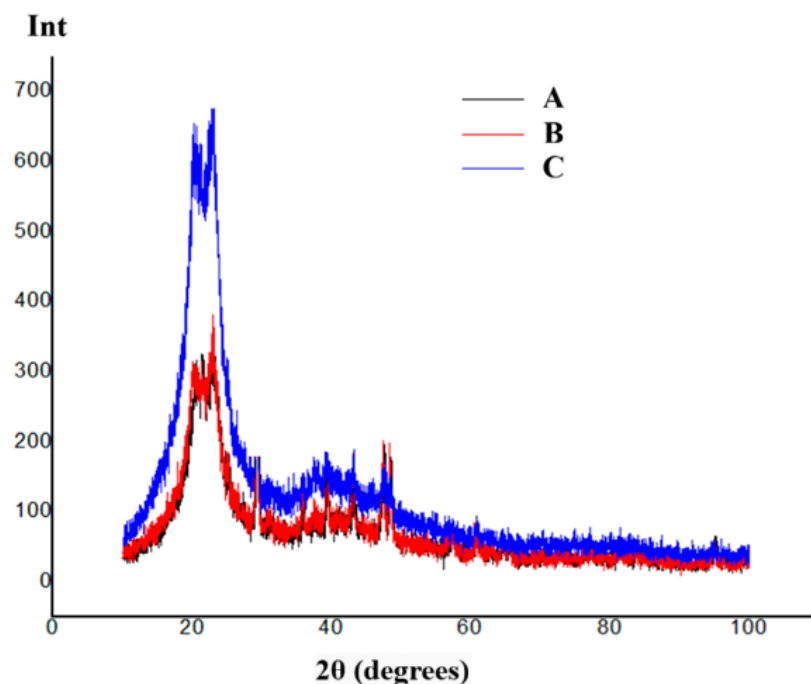


Figure 11. XRD curves of sustainable polymer composites based on the PA6 agglomerate modified with humic substances 0.5% wt. content: A—1% wt. MW-PA CB10 carbon masterbatch, B—3.5% wt. MW-PA CB10 carbon masterbatch, C—5% wt. MW-PA CB10 carbon masterbatch.

This pattern in the change in crystallinity of the modified PA6 waste agglomerate is confirmed by the DSC analysis data on the level of the crystal structure when changing the amount of MW-PA CB10 carbon masterbatch—Figure 12. On the DSC curves, there is a maximum endotherm in the range of $\sim 170\text{--}185\text{ }^{\circ}\text{C}$, characteristic of PA6 melting. The enthalpy of 100% crystalline PA6 is typically reported as 188 J/g [44]. Table 6 shows that the crystallinity of composites based on the PA6 waste agglomerate with humic substances at 0.5% wt. increases to 3% MW-PA CB10 carbon masterbatch at 33.9% and then decreases to 27.3%.

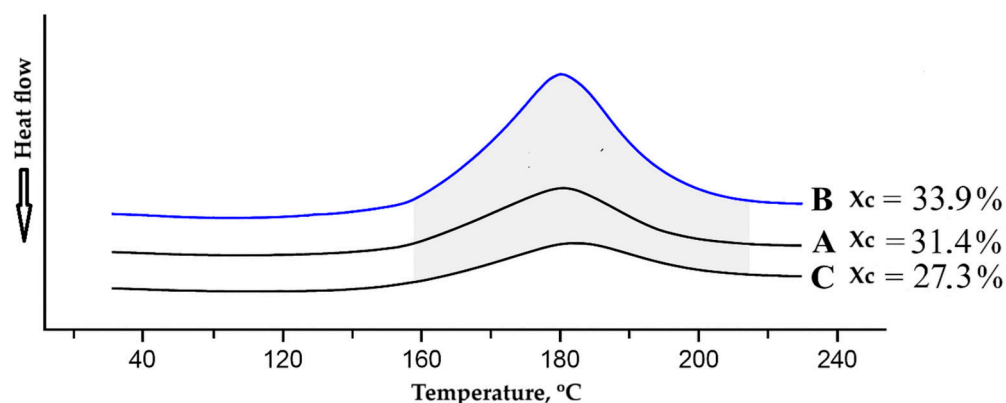


Figure 12. DSC curves of sustainable polymer composites based on the PA6 agglomerate modified with humic substances of 0.5% wt. content: A—1% wt. MW-PA CB10 carbon masterbatch, B—3.5% wt. MW-PA CB10 carbon masterbatch, C—5% wt. MW-PA CB10 carbon masterbatch.

Table 6. Thermal properties from DSC curves of sustainable polymer composites based on the PA6 agglomerate modified with humic substances of 0.5% wt. content.

Composite	$\Delta H_f, \text{J/g}$	$X_c, \%$
1% wt. MW-PA CB10 carbon masterbatch	54.8	31.4
3.5% wt. MW-PA CB10 carbon masterbatch	58.9	33.9
5% wt. MW-PA CB10 carbon masterbatch	43.0	27.3

The composition of the sustainable polymer composites based on the PA6 agglomerate modified with 0.5% wt. humic substances and 2–3.5% wt. MW-PA CB10 carbon masterbatch can be recommended for reuse in traditional PA6 applications for the production of technical products. In fact, the formation of a layer of humic substances in the PA6 matrix during primary modification decreases the contact angle and increases surface energy, thereby improving adhesion with another polar modifier, MW-PA CB10, and enhancing the strength characteristics of the sustainable polymer composites [45]. The design of sustainable polymer composites based on the PA6 agglomerate modified by 0.5% wt. humic substances and 2–3.5% wt. MW-PA CB10 carbon masterbatch was used for general technical parts.

4. Conclusions

Thus, the article presents a systematic study of the combined modification of PA6 waste agglomerates with various types of carbon materials to enhance the technological and mechanical properties of sustainable polymer composites. Various carbon materials were studied: masterbatch for polyamides MW-PA CB10, brown coal humic substances, coke residue from pyrolysis, a mixture of plastic waste, and finely dispersed coal enrichment waste (filter cake). Structural and morphological analysis of the studied carbon materials showed that, within the framework of further modification of the PA6 waste agglomerate, they should perform different functions related to their distinct morphology and chemical

composition. Thus, humic substances can act as functional modifiers and compatibilizers due to their nanodispersity and a wide range of active chemical groups (hydroxyl, carboxyl, peptide, etc.). In contrast, coke pyrolysis residue and coal enrichment waste will act as a functional filler to improve the strength properties of the complex. As part of the study on the effect of modifying carbon materials on the complex technological characteristics of sustainable polymer composites based on the PA6 waste agglomerate, the distinct impact of the studied carbon materials was demonstrated. Thus, humic substances improve the technological properties of sustainable polymer composites based on the PA6 waste agglomerate by increasing the melting temperature and MFI while reducing the density. It should be noted that the functional effect of humic substances increases in the order $HS1 < HS2 < HS3$, which is due to the growth of a wide range of active chemical groups (hydroxyl, carboxyl, peptide, etc.) during the oxidation of the initial brown coal. In contrast, the coke residue from pyrolysis and the coal enrichment waste served as fillers, increasing the density and MFI of the sustainable polymer composite.

As part of the study of the effect of carbon material modification on the complex technological characteristics of sustainable polymer composites based on the PA6 waste agglomerate, it was shown that all carbon materials studied, except for coke residue, improve their strength. The optimal content of different types of humic substances is 0.5% wt., while the impact strength and breaking stress during bending increase in the order $HS1 < HS2 < HS3$, which is associated with an increase in the functionality of humic substances during the oxidation of brown coal.

The scientific significance of the study is associated with the establishment of a cause-and-effect relationship between the degree of brown coal oxidation, the composition of functional groups of humic substances ($-COOH$, $-OH$, etc.), and intermolecular interaction with amide groups of PA6, which provides an increase in the mechanical and technological characteristics of the compositions of the secondary PA6 agglomerate. This is recorded by the consistent data of XRD/ ^{13}C -NMR/IR spectroscopy and DLS/SEM/EDS analyses. The role of humic substances as “functional compatibilizers” is also shown; nanodispersed particles with high polarity enhance the interfacial adhesion in the PA6–humic substance system, which leads to an increase in the impact strength and fracture stress during bending of the compositions of the secondary PA6 agglomerate. In fact, for the first time for the secondary PA6 agglomerate, it has been shown that the combination of small amounts of oxidized humic substances at the level of 0.5% by weight as a functional additive with a masterbatch (2–3.5%) forms controlled crystallinity and strong interfacial H-bonds, which leads to a more than twofold increase in impact strength and a significant increase in flexural strength of secondary PA6 agglomerate compositions without the use of glass fiber or expensive nanofillers.

The practical significance of the study is associated with obtaining ready-to-use formulations of secondary PA6 agglomerate compositions with joint modification with humic substances in an amount of 0.5%wt. and masterbatch MW-PACB10 in an amount of 2–3.5%wt., providing materials with increased impact strength from 23 to ~ 48 kJ/m² and bending fracture stress from 115 to ~ 135 MPa, which allows returning secondary PA6 waste to the “traditional areas of primary PA6” in the manufacture of general technical parts and products. The study also offers an alternative to high-cost glass fiber and carbon fiber in the form of the use of cheap and available carbon resources (humic substances from brown coal, enrichment waste, pyrolysis coke), thereby reducing the cost of the composite and increasing the share of PA6 waste reuse.

Combined modification of the PA6 waste agglomerate by humic substances at a content of 0.5% wt. in the range of carbon masterbatch MW-PA CB10 content 2–3.5% wt. significantly improves the sustainable composite’s strength properties, allowing it to be

recommended for reuse in traditional primary PA6 industries for the production of general technical parts.

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