Carbon materials as fillers for polymer matrix composites

J. Stabik [a], M. Rojek [a], Ł. Suchoń [a,*], K. Mrowiec [b]

[a] Division of Metal and Polymer Materials Processing, Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland

[b] Paint and Plastics Department, Institute for Engineering of Polymer Materials and Dyes, ul. Chorzowska 50A, 44-100 Gliwice, Poland

* Corresponding e-mail address: lukasz.suchon@polsl.pl

ABSTRACT

Purpose: Paper presents different types of carbon materials used as modifiers for polymer matrix composites. The article contains summary description of the available varieties of carbon materials from brown and hard coal to the carbon nanotubes and fullerenes.

Design/methodology/approach: The aim of the publication is to present different forms of carbon materials, their origins and ways of creation. Paper summarizes also basic properties and possible applications of carbon materials as components of engineering polymeric composites.

Findings: Paper especially focuses on types of hard coal (mine coal) as potential fillers for polymers. These materials and their properties and applications were studied in detail by the authors in previous researches.

Research limitations/implications: Analysis of the literature and authors' own research results indicate that carbon materials as fillers can essentially improve many different properties of polymer matrix composites but still have to be extensively searched to fully evaluate their characteristics and possible applications.

Practical implications: Particular attention should be directed to the use of mined coal as a properties modifier of polymers because of its interesting properties, low prize and availability in Poland.

Originality/value: New types of carbon materials as polymer fillers, their properties and application possibilities are presented.

Keywords: Polymers; Composites materials; Fillers; Coal; Engineering materials

Reference to this paper should be given in the following way:

J. Stabik, M. Rojek, Ł. Suchoń, K. Mrowiec, Carbon materials as fillers for polymer matrix composites, Archives of Materials Science and Engineering 53/1 (2012) 29-37.

MATERIALS

1. Introduction

Elemental carbon is the most universal of elements of the periodic table and marked as C in this table. Elemental carbon in chemical compounds have hybridization sp, sp^2, sp^3 and create single or multiple covalent bonds with other carbon atom or with heteroatom. Carbon atoms with sp^2 or sp hybridization possess non-hybridized orbital p which are capable to forming π bond between p orbital of two carbon atoms. In effect it gives, together with sigma bonds formed by sp^2 or sp orbital multiple bond, which allows to create a variety of chemical compounds. This

element also allows for creation of multidimensional structures of substances that have a very wide variety of physical and chemical properties [1]. Characteristic properties of carbon are presented in Table 1.

Table 1.
Basic properties of elemental carbon [2]

Symbol, atomic number	C, 6	Melting point	3820 °K 3546 °C
Atomic mass	12,0107 u	Specific heat	710 J/(kg*K)
Standard atomic weight	70 (67) pm	Density	Depending on a variety

Carbon as an element of such importance isn't at the same time the substance with the largest presence in the earth's crust. As a part of it occupies the 12th position, behind oxygen, silicon, iron, or hydrogen. The carbon content in the earth's crust in all its forms is estimated at only 0.09%. At the same time, despite of such a small content it plays very important role in the nature. Carbon compounds are essential building blocks of all organic matter including plants, animals and humans.

As it was mentioned essential element C in nature is directly caused by its presence as the most important component of living nature. At the same time it should be noted that elemental carbon is a fundamental element of rocks of organic origin. While carbon-containing rocks are generally associated with the fuel it is essential to mention that the elemental carbon also occurs in many non-flammable minerals [2]. The most important inorganic minerals which contain carbon in their structure or their compounds are carbides which occur in meteorites, as well as carbonates, such as [3]:

- Calcite and aragonite $CaCO_3$,
- dolomite $CaCO_3*MgCO_3$,
- magnesite $MgCO_3$,
- siderite $FeCO_3$,
- carbonates of strontium, barium etc.

Without a doubt, the initiation of rapid development of civilization have given various forms of carbon from the charcoal as the first material used for smelting bronze to coal and oil for industrial technology development for production of electricity and mechanical energy. Not without significance is the fact that various forms of carbon also allowed extensive progress in the field of materials science, chemistry and medicine [1].

Last twenty years is a living example of the dynamic development of both various types of polymeric materials is also derived in large part of fossil fuels as well as carbon fillers.

As a filler we know materials which task is to change or improve basic material properties such as polymeric or metallic matrixes [4].

It should be noted that mechanical strength between atoms in C-C bond is the largest from any known in nature. This allows for creation of natural and synthetic materials with amazing mechanical, electrical or biological properties [1].

1.1. Classification of carbon materials

There are many ways of possible classification of carbon materials. Carbon materials diversity is direct result of possibility of creation specific atomic bonds. External conditions such as pressure or temperature have direct influence on creation of carbon materials. It is worth to note that most of a wide range of these materials is in less or more extend present in the nature. However the basic is classification to natural and synthetic materials. Another way of classification is to distinguish basing on crystallographic structure. This classification is as follows:

- allotropic carbon forms:
  - diamond,
  - graphite,
  - fullerenes,
  - nanotubes,
  - glassy carbon,
  - carbins,
- amorphous form of carbon:
  - soot.

There is also another classification used for mined coal. Representatives of this group are hard coal, lignite and anthracite.

In the world of science intensive dispute takes place about possible ways of carbon materials classification, but without a doubt, all of the above mentioned forms belong to the wide group of materials which structure is determined by presence of C element [3, 5].

1.2. Carbon engineering materials

Diamond

Known historical applications of natural diamonds goes back to 300 BC, when diamond was used as the material for manufacturing process, in particular for engraving tools. In next ages the mineral was used usually in jewellery. Afterwards, in 1773, it was also applied as cutting tool used in the precision turning process. In the evolution of the application of natural diamond is also necessary to underline its essential contribution to the development of the wider mining and mining-related work and working with rocks. Milestone was the use a natural diamonds as material for drilling crowns in mining industry as well as to make vertical borehole in the ground. Among the broad spectrum of its usages must also be distinguished diamond wheel with resin matrix developed by Krupp in 1928 [6, 7].

Despite universality of possible applications of natural diamond as a material for enhancing performance of cutting tools, both monolithic and composite, there are some limitations. The main limitation is the lack of natural crystals of sufficient size and relatively high price of its powders. Currently, the technical use of natural material is only 10% of its general purpose and the remaining 90% are synthetic diamonds [7].

Among the methods of manufacture of synthetic material, one can specify the following: high-pressure sintering method that allows to obtain polycrystalline material and the method of CVD (Chemical Vapour Deposition). CVD method allows to obtain thin layered diamond film on large surfaces, and provides simultaneous maintaining chemical purity and crystallographic structure [7, 8].

Basic properties of diamond

Diamond is the hardest material known to man. Hardness of diamond specified on Mohs scale is 10. It is an allotropic variety

of coal, and is meta-stable at ambient conditions and at elevated pressure is characterized by persistence. Diamond crystal structure is a regular wall centred cell with network parameter a = 0.3567 nm. Electrons in diamond are very excited. This allow for forming σsp^3. Valence electrons of carbon atoms in hybridization sp^3 generate four equally acceptable covalent bonds of σ type. Angles between them equal to 109° 28 `and are directed from the centre of the apex proper tetrahedron. The content of sp^3 bonding in diamond is about 86%, while the plane <111> has the largest packing of carbon atoms.

The main disadvantage of very high hardness of diamond is its fragility. Fragility of diamond is directly connected with presence of plane of dense packaging of atoms. Plane <111> can be called a slippage plane.

Diamond as material has low resistance to temperature in air (alotropic transformation into graphite occurs in about 700°C). In anaerobic conditions transformation temperature increase to 1500°C.

In addition to high hardness, diamond materials have another very important properties, they are excellent dielectric and poses high heat conductivity. Value of dielectric constant for diamond ε equals 5.5. Presence of prohibited area in Bad module is characteristic for this material. Heat conductivity of diamond materials is about 2000 W/m*°K. It should be say, that transformation temperature and another properties are strongly dependent from chemical purity of material [6, 9, 10].

Pressure-Temperature (P-T) phase equilibrium of carbon

With the development of modern technology, techniques, and in particular the use of high and ultrahigh pressure, it was possible to carry out the process of transformation of graphite into diamond [6, 7].

Structure of diamond materials is thermodynamically phase meta-stable in each temperature. This condition holds for atmospheric pressure values. This behaviour is the result of higher enthalpy of diamond than graphite. This situation is the reason why the free energy G→D>0. Allotropic transformation may only occur when the condition (free energy G→D<0) is fulfilled. Figure 1 shows the P-T phase equilibrium system of carbon [11].
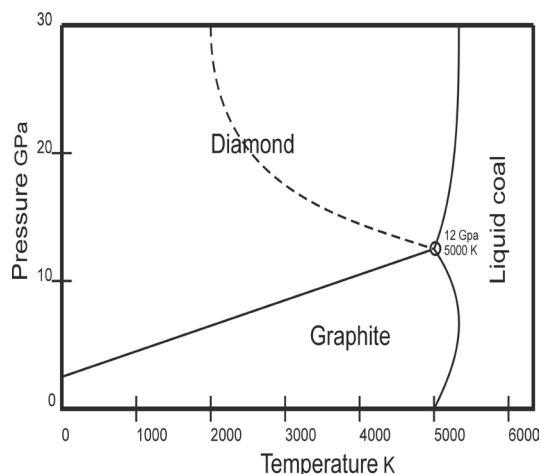

Fig. 1. Phase equilibrium system of carbon

Methods of preparation and use of synthetic diamonds

At present, there are several methods for producing synthetic diamond materials, among which include mainly:

- high-pressure method – synthesis of diamond powder by high-pressure process is conducted at a temperatures about 1330°C to 1630°C , with pressure ranging from 4.5 to 7.7 GPa. High pressure manufacturing process of this diamond powder from graphite feedstock requires using special metal alloys as catalysts;
- low-pressure method – basic methods for manufacturing diamond layers are [6, 12]:
  - PVD method – a method of physical vapour deposition from gas phase;
  - CVD method – a method of chemical vapour deposition from gas phase.

Of the two main methods of synthetic diamond producing from graphite still basically of the main importance is the high-pressure method. At the same time it should be noted that the popularity of low-pressure methods is still growing. Also, graphite as the starting material is increasingly being replaced by other precursors such as e.g. polymer resins, hydrocarbons and fullerenes. Change the precursors as well as modern production methods are designed to obtain a material with the greatest possible particles sizes without impurities and defects, and with high mechanical properties [6].

Graphite

Another widely used carbon material is graphite with all its types. This material is commonly used, as has been previously) reported as a precursor to obtain the synthetic diamond material. Multiple uses of graphite are not limited to the production of diamond. This material is commonly used in the manufacture of electrodes, bearings, crystallisers, seals and many other. It is also applied as a filler for rubber and polymeric materials.

Popularity of graphite as engineering material is due to its excellent electrical, thermal and lubricating properties. Because of these combination of many properties it is one of the widest applied materials in industry [5, 13].

Structure and properties of graphite

Graphite is an allotropic variety of coal. It crystallizes in two systems, hexagonal and rhombohedral. Graphite crystal structure is a flat equilateral network in which corners carbon atoms are arranged. Distances between atoms in the ideal network are 0.1427 nm. At the same time translation of a flat network is a1 = a1 = a1 = 1.246 nm, while the angle between them is equal to 60°. It is possible to determine the area of the hexagonal network by using appropriate equations. Network of graphite crystal is shown in Figure 2 [5, 13].

Built of elemental flat network consist of two carbon atoms within each of them are still on the three carbon atoms that are connected with them by double electron bonds. Hybridization of carbon atom in bonds is sp^2, whilst bond type is σ. It should be noted that these bonds are very strong. Molecular orbitals have shape of asymmetric rotating loop and are arranged at an angle of 120° with respect to each other [13].

Sharing of electrons present in the graphite layer allows for electrical properties like in metals. Electron spins contained in a

flat grid of graphite have antiparallel alignment and electron cloud does not fully overlap.
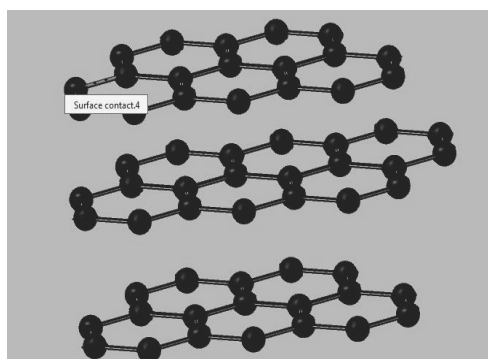

Fig. 2. Expanded graphite crystal [13] hexagonal

The structure of rhombohedral graphite is three-layered with repetition of layer ABC. Percentage of rhombohedral graphite in whole volume of material is not constant, and its concentration strongly depends on the crystallization degree [14].

There is a possibility of elimination of rhombohedral form by heating. Heat treatment causes transformation of rhombohedral form to hexagonal. This process occurs at temperature range from 1330°C to 1530°C. It is worth to say that natural rhombohedral graphite transforms only at the temperature about 3030°C [13, 15].

The nature of the graphite structure is characterized by the presence of strong bonds that exist in the network while the bonds between planar layers are extremely weak. Electrical conductivity parallel to the layers is high while in the perpendicular direction practically does not exist [13]. Table 2 presents some physical properties of graphite mono-crystal.

Table 2.
Physical properties of graphite monocrystal [13]

Property	Unit	In direction		Anisotropy factor
		a	c	
Relevant electrical resistance	μΩ*m	0.5	10000	20000
Heat conductivity	W/(m*°K)	400	80	5
Tensile strength	MPa	20000	-	-
Modulus of elasticity	GPa	1000	30	33

Application of this material as a substitute of many metallic materials for production of cathodes and electrodes gives significant prolongation of utilization time and decreases costs of process as well as reduces technological downtimes.

Natural graphite

Natural graphite is a mineral with shiny black or steel colour form containing in its composition from 2% to 80% of elemental carbon.

According Mantella [13] graphite can be divided according to its structure to:
• flake graphite,
• crystalline graphite,
• amorphous graphite.

In addition to this classification there is also a way of designation of natural graphite directly linked with the mining place of the mineral, such as: Ceylon, Madagascar, Siberia, Canada and Mexico graphite.

The natural form of the flake graphite occurred in some crystalline rocks such as gneiss and carbon shale.

Crystalline form in nature occurs as a vein or agglomeration in the shale and limestone rocks.

Amorphous graphite, in fact the fine crystalline form of graphite, is contained in rocks showing low degree of metamorphism like shale.

It should be noted that there are many ways and attempts to systematize natural graphite. This doesn't change the fact that all species of graphite contain mineral contaminants such as: crystalline shale, mica, or quartz. These impurities are undesirable material, particularly in use mine graphite as a starting material for the manufacture of brushes for electric motors or lubricants and seals.

Natural graphite is manufactured by mineral enrichment method. The main methods include flotation processes and method for sorting in an air stream. Carrying out pre-treatment process allows for obtaining a material with a purity of 99%. Graphite material containing impurities of less than 1% can be obtained by chemical treatment process or heating in a stream of gas that forms volatile compounds with impurities. Material of very high purity is obtained by heat treatment at temperatures from 2500°C to 2800°C.

High temperature processes make it possible to further reduce pollution and partially to order the structure. These are the positive aspects of processing and there are also adverse effects.

Quality evaluation of natural graphite is dependent on the ash content. It is possible also to prove that materials coming from different fields differs in some technological properties, despite similar technical properties [16].

The natural graphite is characterized by the structural anisotropy and physical properties. It also contains mineral admixtures. So its processing is necessary in order to obtain high purity material. It is used as a material for the manufacture of electro-conductive brushes, sliding bearings used in machine building, and as a lubricant or filler of polymer.

Synthetic graphite

Synthetic form of graphite, also called electro-graphite is produced in high-temperature processes. Precursors used for the graphitization manufacturing process to obtain this material are: anthracite and various types of cokes: pitch coke, petroleum coke or coke.

The level of structure ordering in obtained electro-graphites depends strongly on the raw materials as well as on the temperature of the ongoing process.

Main properties of this material are:
• Very high resistance to alkali,
• Good lubricant properties,
• Low sulphur content,

- Very good heat and electrical conductivity,
- Low thermal expansion.

Quantity of ash depends strongly on used precursor and its purity. It ranges from 0.1% to 11%.

Very good resistance to sodium and potassium is especially important feature of electro-graphite. It makes possible to produce cathodes and electrodes for devices working in destructive environments of Na and K [13].

Fullerenes and carbon nanotube

Both fullerenes and carbon nanotubes are allotropic forms of carbon. They both are solid materials. They have a molecular structure, in contrast to diamond and graphite, which creates a crystallographic structure.

The history of these carbon nanostructures started in 1985 after the discovery of carbon molecules whose construction consisted of 60 atoms of C [17]. The shape and arrangement of bonds between atoms of this new carbon molecules looks like football. Basically fullerenes' molecule is a sphere consisting of a sufficient number of clusters in the shape of hexa- or pentagonal.

The first observed molecule of this newly discovered form of carbon was fullerene C60 [17, 18].

The next stage of discovery of these nano-structural forms of allotropic coal was carbon nanotubes discovered by Ijima in 1991 [18]. It should be noted that this date is rather time entry into the canon and the history of modern science, because the form of a carbon fibre were tested in 1889.

However, observation of nanostructured forms of this type is carried out from 50 years of the twentieth century, since the invention of the electron microscope [19].

Fullerenes

Molecules of coal named fullerenes can be defined as: "*multiwalled cages made from carbon atoms in trigonal hybridization which contains 12 pentagonal walls and (n/2-10) hexagonal walls wherein n≥20*" [5].

Researches carried in the recent years show that group of „carbon balls" include many of its kinds. The most popular of them are:

- Standard fullerenes,
- Giant fullerenes,
- Egzohedral fullerenes,
- Endohedral fullerenes,
- Hetero-fullerenes,
- Nano"onions".

This classification shows only main models of fullerene nano-molecules. In this categorization have not been given different subgroups of mentioned structures because of large their number.

Methods of fullerene preparation

Preparation of fullerene structure is connected with condensation of coal gas. Coal gas formed as coal plasma in high temperature process. Because of the wide range of this subject, this process will not discussed here. Among of many method of formation fullerenes , the following can be distinguished:

- laser method,
- electric arc method by Kratschmer and Huffman,
- flame method.

The most important of this method of fullerene preparation is electric arc process. This process allow for preparation of large quantities of material [17, 18].

Carbon nanotubes

Graphene molecule with hybridization of carbon atom sp^2 is use as a precursor for preparation both fullerenes and carbon nanotubes. Creating of cylindrical structure of nanotubes is possible by rolling a plane consisting of graphenes.

There is a possibility of preparation three basic types of single walled nanotubes:

- zig zac,
- chair,
- chiral.

Type of obtained structure depends on direction of graphene plane rolling, which is defined by vector of direction with coordinates m, n. It should be said that m, n are total positive numbers. The coordinates of the vector or cross allow for identification of given single-walled nanotubes.

Diameters of carbon nanotubes range from 0.3 nm to 2.6 nm, nanotube with larger diameters are thermodynamically unstable. These types of carbon nano-material possess good electrical and heat conductivity properties. These properties are result of their structure. Most of nanotubes have semiconducttive properties; in some cases depending of the structure they possess also metal conductivity [20].

There is a possibility of to take advantages of these properties in electronic in semiconductors which replace silicon electronics.

Carbon nanotubes preparation methods

Carbon nanotubes as well as fullerenes could be obtained by several methods such as:

- electric arc method,
- laser method,
- CVD method.

At the same time regardless of the methods used to manufacture the resulting product can take two basic forms:

- a form of tumbling,
- a form of evenly arranged rows.

Carbon nanostructures are used in wide range of applications as engineering materials. Ranging from electronics as semi-conductor materials through the fillers of polymers and textiles to military applications. The branch of knowledge and science concerning carbon materials promise a rapid development of modern technologies.

Carbon black

Carbon black is very important material widely used as polymer filler. It is amorphous form of coal, which usually consist of spherical particles of elemental carbon. Size of these molecules is less than few dozen nanometers. Particles create agglomerations with different spatial configuration. Structure and configurations of particles influence properties of carbon black.

The genesis of obtaining carbon black is mainly based on incomplete combustion of carbonaceous materials. The main precursors include: wood, coal, natural gas and hydrocarbons. The basic production methods for this material include: furnace method, lamp method, and now more widely used plasma method.

The amorphous form of the element C is widely used in industry, mainly as filler in rubber components during rubber processing and in paints. Carbon black is also used for the manufacture of dry cells in the electrical industry, the pharmaceutical industry or in the manufacture of paints and varnishes [13, 17, 21].

Mined coal

Describing technical uses of carbon materials the role of mined coal in many industry branches cannot be forgotten. Wide areas of its application are result of mined coal universality. Their industry uses is role of precursor for chemical synthesis for preparation engineer carbon materials as well as industrial As indicated earlier works of authors there is also the possibility of using hard coals as polymer fillers.

Of the many types of metamorphic rocks most important are: coal, lignite, peat, or shungites, anthracites. Genesis of forming these minerals are biochemical processes. The basic process is carbonization of biological substrate into rocks with different degree of carbonitization.

Basically hard coals have many features among which the most important are carbonitization degree, calorific value, ash content and sulphur content. The last of mentioned parameters is undesirable and causes the necessity of pre-enrichment. This process could be carried by flotation method or by chemical method in order to remove impurities. The main advantage of this material is very large content of elemental carbon C. Multiplicity of hard coal variety allowed their widespread use in both technology and everyday life [2, 3, 22-24].

2. Experimental

2.1. Materials

Polyamide 6 with trade name „Nevimid 6 MLD Naturale" produced by „Nevicolor" (Italy) was used as a matrix for all prepared formulations. Table 3 presents basic properties of used polyamide.

Table 3.
Basic Properties of Nevimid 6 MLD Natural

Property	Value
Yield stress, MPa	90
Strain at break, %	100
Modulus of elasticity, MPa	3000
Izod impact strength, J/m	45
Vicat temperature (Method A), °C	215
Rockwell hardness, R scale	116

Two different types of powdered hard coal were used as fillers:
- hard coal type 33-34 produced by 'Bolesław' mine (Poland), milled and sieved on sieve with mesh diameter 0.035 mm (assigned as 1B);
- hard coal type 35 produced by 'Zofiówka' mine (Poland), milled and sieved on sieve with mesh diameter 0.035 mm (assigned as 2Z).

Basic physical properties of applied hard coals are presented in Table 4.

Table 4.
Basic physical properties of coal 1B and 2Z [15]

Properties \ Filler	Coal 1B	Coal 2Z
Density, g/cm^3	1.3	1.33
Contents of element C, %	84.22-86.10	88.46

Mechanical processing, leading to final particle size of fillers, was performed with help of following machines:
- hammer crusher,
- disintegrator mill,
- ball mill.

Very important was to keep humidity of hard coal during grinding in the ball mill under 2%. Because of the influence of ball milling parameters on final state of filler, constant parameters of grinding for both coal types were kept.

Filled polymeric compositions were prepared using laboratory two-screw extruder with mixing zones. Samples were prepared with fillers dosing at 7%, 14%, 21% weight contents. Mixing was performed with the following process parameters:
- temperature of extruder zones: 220-230-240°C;
- temperature of extrusion die: 240°C;
- extruder screw speed: 6 rpm;
- extrusion die diameter: 3 mm.

Extrudates in shape of rods were next granulated on laboratory knife granulator. Obtained in this way granulate was then used in MFR investigations.

2.2. Research methods

Particle size analysis

Sieve analysis was made in aim to evaluate particle size distribution. Analysis was performed on vibratory sieve particle size analyser. Sieves with mesh diameter from 0.1 to 0.035 mm were used. Analysis was made with dry method.

Density measurement

Measurements were made according to Polish standard PN-92/C-89035 using displacement method. Analytical balance type XS produced by Mettler Toledo was used. Basic density conditions were:
- temperature: 21.2°C;
- immersion liquid: distilled water.

Immersion liquid density was measured with aero meter type Densito 30P. Temperature was measured with precise mercury thermometer.

Melt flow index measurement

Measurements of melt flow index were realized according to Polish standard PN-93/C-89069. Investigations were made with Dynisco plasrometer S4000. Measurement was made in following conditions:
- environment temperature: 25±1°C,

- cylinder temperature: 230°C,
- sample heating time: 240 s,
- time of sample extrusion: 6 s,
- piston and dead weight mass: 2160 g.

Taking into account test conditions, measured values of melt flow index may be assigned as $MFR_{230/2,16}$.

Viscosity calculations procedure

Plastometer used to MFR measurements may be compared to capillary rheometer. In order to calculate viscosity on MFR value basis two quantities have to be evaluated: shear rate and shear stress.

Viscosity was determined using generally known formula, which connected shearing stress with shear rate:

$$\eta = \frac{\tau}{\dot{\gamma}} [Pa \cdot s] \qquad (1)$$

Determined in this way viscosity values are approximate because it was not possible to perform Rabinovitsch-Mooney's or Bagley's corrections. Apart from this comparison of achieved results was informative.

2.3. Results and their analysis

Particle size analysis

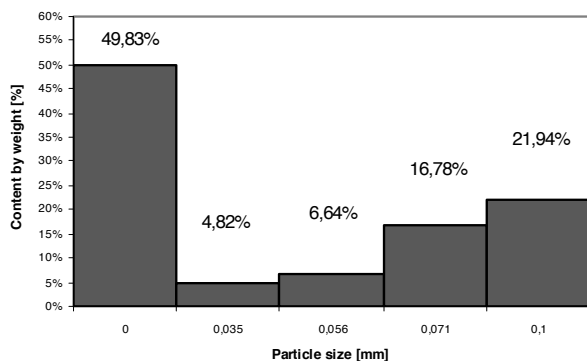Particles size distribution charts for both coal types are presented in Figures 3 and 4.

Fig. 3. Graphical interpretation of particle size distribution for coal 1B

As can be seen in presented curves, for both hard coal types, the biggest amount of particles had equivalent diameter below 0.035 mm. Hard coal 2Z contained more particles in this range. Because about 50% of particles fell in the 0-0.035 mm range it is planned to perform additional, more precise analysis of particle size distribution.

Density results

Results of density tests for pure polyamide and all composites are given in Table 5. Mean values and standard deviation were calculated into Table 5.
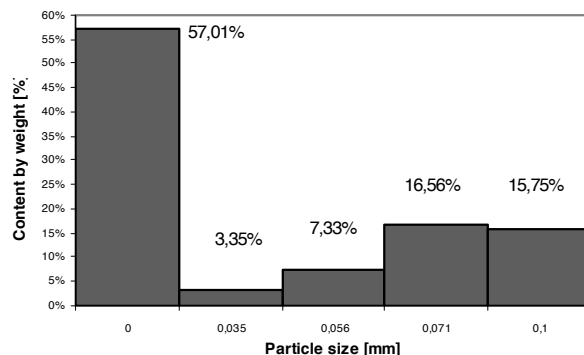
Fig. 4. Graphical interpretation of particle size distribution for coal 2Z

Table 5.
Average density values for polyamide filed with hard coal

Composite designation	Coal content	Density ρ, g/cm³	Standard deviation
PA	-	1.134	0.003
1B	7%	1.145	0.002
1B	14%	1.166	0.001
1B	21%	1.186	0.004
2Z	7%	1.141	0.0006
2Z	14%	1.151	0.0006
2Z	21%	1.162	0.0015

Composites density increases together with filler content increase. It is obvious result of higher filler than matrix density.

MFR results

Results of melt flow index measurements for pure polyamide and all composites are given in Table 6. Mean values and standard deviation were calculated into Table 6.

Table 6.
Comparison average value of MFR

Composite designation	Coal content	Massive flow rate MFR, g/10min	Standard deviation
PA	-	19.95	0.07
1B	7%	17.23	0.80
1B	14%	15.37	1.45
1B	21%	13.43	3.33
2Z	7%	17.03	0.21
2Z	14%	14.00	0.26
2Z	21%	11.00	0.78

Figure 5 shows dependence of melt flow index on type and contents of hard coal particles.

Obtained results showed that mass flow rate (MFR) decreased with volume content of carbon fillers increase.

Viscosity results and their analysis

Viscosity was determined according to point 2.2.4. In Table 7 are given results of volumetric rate of flow, shear rate and viscosity calculations.
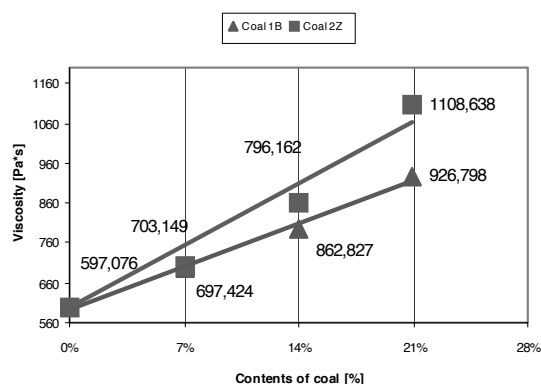
Fig. 5. Dependences of composites viscosities on hard coal contents

Table 7.
Results of volumetric rate of flow, shear rate and viscosity calculations

Probes	Volumetric rate of flow, cm³/s	Shear rate, s⁻¹	Viscosity, Pa*s
PA	0.0293	32.469	597.076
1B7%	0.0251	27.797	697.424
1B14%	0.0220	24.350	796.162
1B21%	0.0189	20.917	926.798
2Z7%	0.0249	27.571	703.149
2Z14%	0.0203	22.468	862.827
2Z21%	0.0158	17.487	1108.638

Dependences of composites viscosities on filler contents are presented graphically in Fig. 5.

As can be seen, viscosity increased almost linearly with filler content for both hard coal type. Slightly higher viscosities were observed for composites filled with hard coal type 1Z. It is probably result of higher content of very fine particles in this type of powdered coal (compare Fig. 3 and Fig. 4). Linear character of observed dependences inclined to compare experimental results with that calculated according to Einstein's theory.

In the Table 8 are given results of relative viscosity calculations obtained from experimental results and according to Einstein's theory.

Table 8.
Results of relative viscosity calculations

Composite designation	Coal content	Experimental relative viscosity	Relative viscosity according to Einstein
PA	-	1.000	1.000
1B	7%	1.168	1.154
1B	14%	1.333	1.311
1B	21%	1.552	1.471
2Z	7%	1.178	1.152
2Z	14%	1.445	1.307
2Z	21%	1.857	1.465

Measured viscosities of composites are higher than predicted by Einstein's theory. Greater differences were observed for composites with 2Z hard coal. Higher viscosities are probably result of irregular shape of hard coal particles.

3. Conclusions

Experimental results and their analysis allow to draw the following conclusions:
- Addition of hard coal particles to polyamide matrix caused essential viscosity increase. Viscosity increased linearly with filler content;
- Higher viscosities were measured for composites with 2Z hard coal particles than for composites with 1B particles;
- Observed viscosity increase was higher than that predicted by Einstein's theory. Einstein's equation modification was proposed to achieve better fitting of experimental results to approximation equation;
- Viscosity measurement results together with particle size distribution results proved that composites with finer particles exhibit higher viscosity values. Comparison of these results showed that for searched composites the main influence on viscosity increase had particles with diameter smaller than 0.035 mm.

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