

Investigation of processing properties of polyamide filled with hard coal

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Materials

ABSTRACT

Purpose: The aim of this article is to present the influence of contents and kind of hard coal used as powder filler on rheological properties (viscosity) of polyamide 6.

Design/methodology/approach: Preparation of composite of polyamide 6 with hard coal was carried out on laboratory twin screw extruder. Extruded composite was granulated and in this form was used for MFR analysis. Taking into account MFR results viscosity was calculated. The influence of filler content on viscosity was next searched.

Findings: Results of research showed that addition of powdered hard coal to polyamide 6 matrix cause pronounced decrease of MFR index. In this way significant increase of viscous flow was observed. It is often observed phenomenon for polymer composite filled with powder materials.

Research limitations/implications: It is necessary to carry out the research with surface modified hard coal with coupling agents which provide better adhesion of polymer matrix to filler.

Practical implications: Hard coal used as a filler in composites makes it possible to gain new and cheaper polymeric materials with many possible applications.

Originality/value: Investigation described in article shows possibility of hard coal application as innovatory filler of polymers. The influence of this filler on rheological properties indicate that processing of these new materials may be accompanied with some problems.

Keywords: Composites; Working properties of materials and products; Hard coal; Engineering materials

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1. Introduction

Nowadays in engineering practice polymers and polymer based composites act to be a commonly used constructional materials. Their comprehensive applications come off from many interesting properties which significantly differ from metals, ceramics or glass characteristics. Processing of high molecular weight materials is in many technologies relatively simple and do

not require big energetic consumption as for example for metals. Unmodified polymeric materials, still widely applied in present industry, often do not fulfil increasing demands concerning mechanical, electrical, thermal, durability and many others properties.[1, 20]

Actually into modern industrial practice are introduced very few new polymers which substantially differ in chemical structure from those which are known for many years. Because of this it is necessary to look after polymer modifications, polymer mixtures

and polymeric composites which can provide materials with improved properties relative to origin polymers. One of widely applied modifiers of polymers are fillers. They are introduced into polymeric matrix to improve its properties (active fillers) or to decrease its price (passive fillers).[2, 3, 21]. Therefore, composite materials with powders or short fibres fillers are more and more significant among construction materials. A popular definition of fillers states that they are small solid particles which are introduced into polymeric matrix at content level higher than 10% by weight. Filler content of polymeric composites processed by injection moulding or extrusion technology may achieve up to 60% by weight. This fact confirms a viewpoint that in this kind of composite a high molecular weight material is rather a filler binder than dominant matrix [4, 5]. Commonly used powder fillers are [6]: quartz sand and quartz flour, chalk, talc, kaolin, glass spheres and glass beads, wollastonite, mica powder, graphite, carbon black and dolomite flour. These days many also nanofillers find new applications. Influences of typical powder fillers incorporated into thermoplastic and thermosetting resins on many different properties were already explored. Influence of hard coal filler on features of high molecular weight materials hasn't been known as well yet.[7] Therefore in Institute of Engineering Materials and Biomaterials, Division of Metallic and Polymeric Materials Processing a research programme on influence of powdered hard coal on mechanical, electrical and rheological properties of thermoplastic polymers was undertaken. Investigations concentrate on influence of content, coal type and particles geometry on mentioned properties.

High performance applications of filled composites require to recognize modification possibilities of mechanical, electrical, thermodynamic, rheological and other classes of properties of polymers with fillers. It enables consciously to choose the proper kind of filler and the proper level of its content. One could not expect that due to addition of a given type of solid particles to polymer matrix it is possible to improve all properties. There is no such a universal filler which positively influences all properties in all applications. Usually appreciable improvements of one or few properties are accompanied by considerable deterioration of other properties [2]. Many disadvantages of fillers addition may also be caused by improper composites preparation and casual effects arising during composites processing. Main deterioration and negative casual effects of using fillers are[8,9]:

- Particles sedimentation, which could be a reason of inhomogeneous structure of material;
- Particles agglomeration, which cause locally inhomogeneous structure of material and in this way decrease of mechanical, electrical and rheological properties in agglomeration region;
- Increase of density;
- Deterioration of processing properties;
- Decrease of dielectric properties in result of humidity absorption;
- Deterioration of mechanical, electrical and rheological properties caused by improper adhesion between particle surface and polymeric matrix.

Fortunately, not all of enumerated deteriorating phenomena occur simultaneously. Changes of rheological properties, which are closely connected with processing characteristics of composite materials, have fundamental meaning for selection of processing technology, processing machine and parameters of technological

process. In literature it is generally accepted that fillers cause negative viscosity increase, what results in higher resistance to flow. On the other hand, positive elastic recovery decrease is observed, what results in lower die swell effect. For most of processing technologies more important is increase of flow resistance of filled polymer in comparison with origin plastic material. It is especially troublesome for high concentrations of powdered fillers. Main technological result of composite viscosity increase is necessity of processing parameters adjustment. First of all pressures and temperatures have to be raised to achieve proper flow velocities, for example in runner system of injection moulding tools and flow channels of extrusion dies. Natural result of increased resistance to flow are also higher torque values needed to drive screws of injection moulding machines and extruders. That extorts from manufacturers necessity of using machine with higher technological parameters and energy consumption.

On the other hand small amounts of filler do not require substantial changes of technological parameters and in many cases allow to substantially modify materials properties. For some fillers, for example platy talc particles [2], it is even possible that viscosity of filled polymer is lower than viscosity of origin material. Improving or deteriorating effect of fillers on rheological characteristics depends on kind of used filler, mainly on particle geometry characteristics such as shape, size and aspect ratio and also on solid particles content [2]. Dynamic development of processing technologies of polymeric materials require to define characteristics which have determinant role in given processing method. Uncomplicated technological probes were firstly widely spread, such as injection of molten polymer into spiral cavity or conical rod pressing. Some of these methods are used also nowadays. One of the methods applied for many years and widely used also nowadays is volume (MVR) and mass (MFR) flow rate index, in abbreviation called also melt flow index [2]. It is defined as a volume or mass of molten thermoplastic polymer extruded in standard temperature and under standard pressure, from standard capillary in 10 minutes time. Pressure is induced by piston loaded with standard weight [10]. Because melt flow rate index indirectly defines viscosity, it is commonly applied by manufacturers to polymers characterisation and by processors to technological parameters setting. To unequivocal interpretation of MVR and MFR values, test parameters (temperature and pressure) have to be given together with tests results. Measurements of melt flow index are performed in equipment called melt plastometer [11]. MFR is calculated on the basis of measured extrudate mass, using the following equations:[10]

For the standard Method A:

$$MFR(\Theta, m_{nom}) = \frac{t_{ref} \cdot m}{t} [g/10min] \quad (1)$$

where:

Θ - temperature of the test [°C],
 m_{nom} - nominal mass of the weight [kg],
 m - average mass of the extrudate [g],
 t_{ref} - reference time [s],
 t - sampling time [s].

For standard Method B:

$$MFR(\Theta, m_{nom}) = \frac{A \cdot l \cdot \rho \cdot t_{ref}}{t} [g/10 \text{ min}] \quad (2)$$

where:

Θ - temperature of the test [$^{\circ}\text{C}$],

m_{nom} - nominal mass of the weight [kg],

A - average piston and cylinder cross-sectional area [cm^2],

t_{ref} - reference time [s],

t - sampling time [s],

l - average measured piston stroke [cm],

ρ - density of tested thermoplastic material [g/cm^3] defined by the following formula (3):

$$\rho = \frac{m}{A \cdot l} [g/cm^3] \quad (3)$$

where;

m - mass of the extruded material with known volume, measured by weighing (g).

Development of processing technologies of high molecular weight materials caused that polymers features, which have direct influence on their behaviour during flow, have to be known. These properties are generally known as rheological characteristics. Viscosity is the most important among them. For simplest materials, called Newtonian fluids, viscosity is also the only material characteristic needed to fully describe rheological behaviour during flow. General form of equation of state for these fluids is following:

$$\boldsymbol{\sigma} = -p\mathbf{1} + \eta \cdot 2\mathbf{D} \quad (4)$$

where:

p - pressure,

\mathbf{D} - tensor of deformation rate,

$\mathbf{1}$ - unit tensor,

$\boldsymbol{\sigma}$ - stress tensor

η - viscosity.

In one-dimensional form, for example for shearing flows, it is known as Newtonian law for fluids:

$$\tau = \eta \cdot \dot{\gamma} \quad (5)$$

where:

$\dot{\gamma}$ - shear rate,

τ - shear stress.

For incompressible bodies equation (4) is known as generalized Navier-Stokes equation. Unfortunately, thermoplastic molten polymers are non-Newtonian in their rheological nature. For this kind of fluids viscosity is a function of deformation rate tensor. Most often it is described as a function of the second invariant of deformation rate tensor (II_D):

$$\boldsymbol{\sigma} = -p\mathbf{1} + \eta(II_D) \cdot 2\mathbf{D} \quad (6)$$

where:

II_D - second invariant of deformation rate tensor.

In one-dimensional form, for shearing flows, it is known as generalized Newtonian law for fluids:

$$\tau = \eta(\dot{\gamma}) \cdot \dot{\gamma} \quad (7)$$

Polymer melts are pseudoplastic in their rheological behaviour. Their viscosity decrease with increasing shear rate. Complete characterisation of high molecular weight materials

viscosity at defined temperature and at known pressure require to determine viscosity dependence on shear rate, which graphic interpretation is known as viscosity curve:

$$\eta = \eta(\dot{\gamma}) \quad (8)$$

A form of $\eta = \eta(\dot{\gamma})$ function which is widely used in literature and very extensively in practice is the so-called 'power law':

$$\eta(\dot{\gamma}) = K \cdot \dot{\gamma}^{(n-1)/2} \quad (9)$$

where K and n are constant fluid parameters. 'K' is called consistency coefficient and 'n' is called the power-law index.

For Newtonian fluid $n=1$, for pseudoplastic fluids, such as polymer melts, $n<1$ and for dilatant materials $n>1$.

In rheometry practice instead of viscosity curve flow curves are used more extensively. The flow curve is graphic imaging of shear stress dependence on shear rate:

$$\tau = \tau(\dot{\gamma}) \quad (10)$$

It is worth mentioning that for most polymer melts it is possible to determine flow curve parameters on the basis of measured flow index value [2,12-14,17-19]. Of course, determined in this way flow curve parameters are only approximate. Observed fillers influence on viscous properties of polymer melts is rather complicated issue. Results of investigations confirm commonly observed regularity that fillers particles introduction into polymeric matrix results in increase of viscous flow resistance. This fact is explained by adhesive forces existing between liquid and solid particles of filler, which have to be overcome, and by additional energy needed to transport solid particles. This phenomena cause additional energy dissipation during composite melt flow. The first theory concerning influence of solid particles on dispersion viscosity was proposed by A. Einstein [2]. For mono-dispersed buoyant spheres in Newtonian fluid his theory predicts that viscosity is linearly dependant on volumetric filler content. Einstein additionally assumed that solid particles content is low that no interactions between particles occur. Best known form of his theory is the formula:

$$\eta = \eta_0 \cdot (1 + 2,5\phi) \quad (11)$$

where:

η - viscosity of dispersion,

η_0 - viscosity of unfilled Newtonian liquid,

ϕ - volume content of solid particles.

In results of many limiting presumptions accepted by Einstein, in real industrial conditions and even in scientific research experiments, Einstein's formula is fulfilled rather rare. Many other researchers tried to achieve better correlation between theoretical and experimental results by modifying proportionality factor 2,5. Most propositions fall in the range between 1,5 and 5,5, depending on kind of searched fluid-solid particles dispersion system.

Einstein's theory was later extended to polynomial form. All of proposed formulas may be expressed in series form [2]:

$$\eta_r = \frac{\eta}{\eta_0} = \sum_{n=0} c_n \phi^n \quad (12)$$

where:

c_n - model parameters

Many theories accepted conception of maximum packing content (ϕ_m) [2]. With this concept equation (13) may be written as:

$$\eta_r = \frac{\eta}{\eta_0} = \sum_0^n c_n \phi_r^n \quad (13)$$

where:

$$\phi_r = \frac{\phi}{\phi_m} \quad (14)$$

Also for filled polymeric dispersions many theories were proposed. Many experimental research programmes were realized, too. As a result a lot of theoretical, empirical and semi-empirical equations describing filled polymers melts viscosity were proposed. In the literature very popular are Mooney's equation (15), or Maron and Pierce's formula (16) [3].

$$\ln \frac{\eta}{\eta_0} = 2,5 \cdot \left[\frac{\phi}{1 - K \cdot \phi} \right] \quad (15)$$

where:

K – empirical constant;

$$\eta = \eta_0 \cdot \left[1 - \frac{\phi}{A} \right]^2 \quad (16)$$

where:

A – empirical constant.

It is worth mentioning that for filled polymeric materials in experimental research and in industrial tests most often in use is Marone and Pierce's dependence (16).

Unfortunately in spite of many proposed dependences, no universal formula exists for different polymeric matrixes, for different solid particles and for wide range of contents. Real polymeric dispersions are still extensively searched in theoretical and experimental projects. At least six factor, which influence viscosity of real filled polymeric melts, are frequently underlined [2]:

- Solid particles of most applied fillers are non-spherical;
- Fillers are characterized by broad particle size distribution;
- Melts of high molecular weight polymers are non-Newtonian liquids;
- Highly filled polymers exhibit yield point;
- Wall slip phenomenon occur during highly filled polymers flow;
- Interactions between filler surface and thermoplastic polymer matrix take place.

Experimental results show that particles diameter has no significant influence on dispersion viscosity in the case of low filler content. Inversely, for high contents of filler, particles size is very important. The bigger are particles the lower dispersion viscosities are observed. Very important is also particles size distribution. It is generally observed that slip phenomenon between layers during shearing flow of dispersion take place. Force needed to induce mutual slip depends on layers 'roughness'. Solid particles present in dispersion determines this roughness. It is possible to modify this phenomenon by using filler with broader particle size distribution. Small particles decrease layer roughness and additionally play role of a 'grease' facilitating layers mutual slip. As it was shown in research of Chong, Christiansen, and Berg, viscosity decrease as results of partial size distribution broadening is not fully covered by theoretical predictions [15]. Additionally, using filler with broad particles size distribution may be the reason of dilatation effect.

This effect lies in viscosity increase with shear rate increase. The phenomenon is especially often observed for dispersions with very high filling degree. It is worth to mention that also agglomerates have significant influence on increase of viscosity. Agglomerates frequently are formed during composition preparation or during flow. Viscosity increase induced by agglomerates presence is caused by the decrease of maximum content. Significant fluid volume is trapped in agglomerates pores and can not be deformed. Loading of polymer melt and other fluids with non-spherical particles may be the reason of additional effects. Most theoretical considerations apply to dispersions filled with ellipsoidal and tubular solid particles [15]. Unfortunately there are not so much publications describing flow of dispersions filled with particles of different shape.

In the present project viscosity of polyamide filled with new type of filler, namely powdered hard coal, was searched. Because of preliminary character of this stage of experimental programme, melt flow index was used as a measure of viscous properties of composites. Viscosity was calculated on the basis of measured index. The influence of hard coal type and content on viscosity was analysed.

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 1 presents basic properties of used polyamide.

Table 1.
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

Table 2.
Basic physical properties of coal 1B i 2Z [16]

Properties	Filler	Coal 1B	coal 2Z
Density [g/cm ³]		1.3	1.33
Contents of element C [%]		84.22-86.10	88.46

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 0.035mm (assigned as 1B);
- hard coal type 35 produced by 'Zofiówka' mine (Poland), milled and sieved on sieve with mesh diameter 0.035mm (assigned as 2Z).

Basic physical properties of applied hard coals are presented in Table 2.

Both types of used coal (1B and 2Z) were prepared in the same manner. Powder of filler with suitable particles size distribution was prepared by mechanical working of hard coal supplied by mines. Both types of hard coal were delivered as pea coal with mean pieces diameter about 50mm. 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. One part of coal (0,5 kg) was ground using 8 parts of balls (4 kg). Grinding time was 15 min.

Filled polymeric compositions were prepared using laboratory two-screw extruder with mixing zones. Composites were prepared in Laboratory of Institute for Engineering of Polymer Materials and Dies, Division in Gliwice (Poland). Samples were extruded using 200g of polyamide 6 granulate and coal powder in amounts sufficient to achieve 7%, 14%, 21% by 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 in Laboratory of Division of Coal Processing and Waste Utilization, Department of Geology and Mining of Silesian University of Technology. Analysis was performed on vibratory sieve particle size analyzer. Sieves with mesh diameter from 0.1 to 0.035mm were used. Analysis was made with dry method.

Density measurement

The next performed test was composites density determination. This test had only ancillary character. Densities of PA6 filled with coal were needed to calculate shear rates on the basis of MFR results. This test was made in Laboratory of Division of Engineering Materials, Main Institute of Mining in Katowice (Poland). Measurements were made according to Polish standard PN-92/C-89035 using displacement method. Analytical balance type XS produced by Mettler Toledo was used. A special ancillary equipment devoted to density measurement was applied.

This equipment allowed to calculate density automatically taking into account weight measurements. 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. Electronically operated equipment made it possible to directly evaluate MFR after sample weight input. Test Method A (eq.1) was used. Extrudate weight was measured using electronic analytical balance WP 50SX/1 preciseness 0.001[g], produced by Radwag (Poland). 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. Shear rate at capillary wall is described by formula [17]:

$$\dot{\gamma} = \frac{32Q}{\pi \cdot d^3} [s^{-1}] \quad (17)$$

where:

Q – volumetric rate of flow;

d – capillary diameter (2,095mm).

Volumetric rate of flow may be calculated taking into account measured MFR value, composite density (ρ) and time of MFR measurement ($t=10 \text{ min}=600\text{s}$).

$$Q = \frac{MFR}{t \cdot \rho} \quad (18)$$

Shear stress on capillary wall may be calculated using following formula (19):

$$\tau = \frac{d \cdot \Delta p}{4l_c} \quad (19)$$

where:

Δp – pressure gradient measured on capillary length;

l_c – capillary length (8,00 mm).

Pressure gradient is equal to pressure generated in plastometer by piston pressing on polymer melt:

$$\Delta p = \frac{4F}{\pi \cdot D^2} \quad (20)$$

where:

F – force acting on melt;

D – diameter of plastometer cylinder (9,55mm).

Assuming that friction force between piston and cylinder is nearly zero, force acting on molten polymer is equal:

$$F = m_w \cdot g \quad (21)$$

where:

m_w - piston and dead weight mass (2160 g);

g – acceleration of gravity.

Because shear stress is constant for all MFR measurements, it is reasonable to calculate it here:

- F = 21.19 N;
- $\Delta p = 0.296 \text{ MPa}$;
- $\tau = 0.0194 \text{ MPa}$.

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

$$\eta = \frac{\tau}{\dot{\gamma}} [Pa \cdot s] \quad (22)$$

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

Results of particles size analysis is shown in Table 3.

Table 3. Particle size distribution of coal 1B oraz 2Z

Coal type	Particle size [mm]	Content by weight [%]	Total content by weight [%]
Coal 1B	> 0.1	21.93	21.93
	0.1-0.071	16.78	38.71
	0.071-0.056	6.64	45.35
	0.056-0.035	4.82	50.17
	0.035-0	49.83	100
Coal 2Z	> 0.1	15.75	15.75
	0.1-0.071	16.56	32.31
	0.071-0.056	7.33	39.64
	0.056-0.035	3.35	42.99
	0.035-0	57.01	100

Particles size distribution charts for both coal types are presented in Figure 1 and 2.

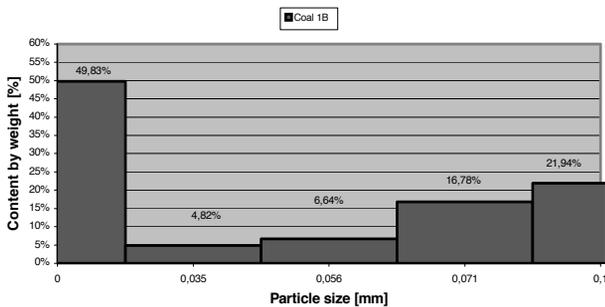


Fig. 1. Graphical interpretation of particle size distribution for coal 1B

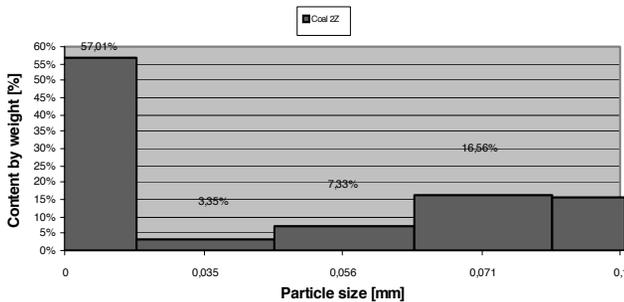


Fig. 2. Graphical interpretation of particle size distribution for coal 2Z

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 4. Mean values were calculated taking into account (Table 4) measurements results.

Table 4. Average density values for polyamide filled with hard coal

Composite	Density ρ [g/cm ³]	Standard deviation
PA	1.134	0.003
1B7%	1.145	0.002
1B14%	1.166	0.001
1B21%	1.186	0.004
2Z7%	1.141	0.0006
2Z14%	1.151	0.0006
2Z21%	1.162	0.0015

Dependences of composite density on filler content are shown in Fig. 3. Results confirmed generally observed regularity that composites density increases together with filler content increase. It is obvious result of higher filler than matrix density.

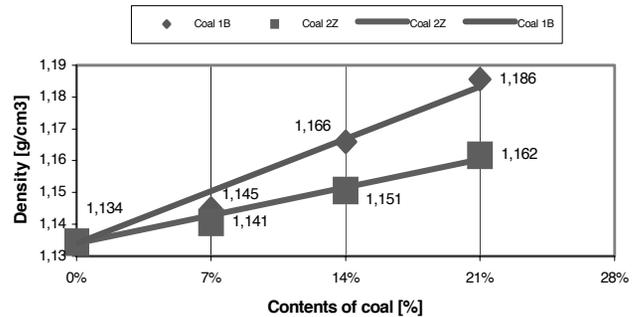


Fig. 3. Influence of hard coal contents and kind of coal on density

Because of ancillary character of density measurements, density results were not further analysed.

MFR results

Results of melt flow index measurements for pure polyamide and all composites are given in Table 5. Mean values were calculated taking into account (Table 5) results.

Table 5. Comparison average value of MFR

Composite	Massive flow rate MFR [g/10min]	Standard deviation
PA	19.95	0.07
1B7%	17.23	0.80
1B14%	15.37	1.45
1B21%	13.43	3.33
2Z7%	17.03	0.21
2Z14%	14.00	0.26
2Z21%	11.00	0.78

Fig. 4 shows dependence of melt flow index on type and contents of hard coal particles.

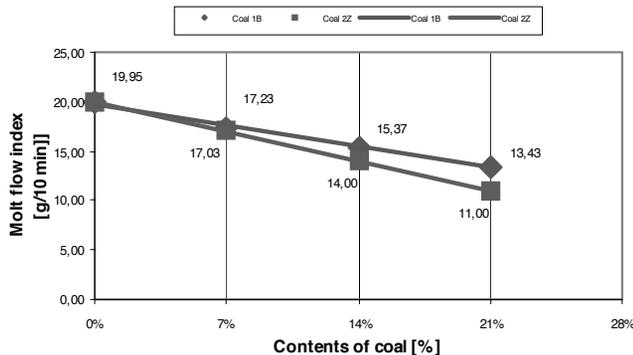


Fig. 4. Influence of content and kind of coal on MFR_{230/2,16}

Obtained results showed that mass flow rate (MFR) decreased with volume content of carbon fillers increase. Because this index was used only as a starting quantity for viscosity calculation, it was not analyzed in detail.

Table 6. Results of volumetric rate of flow, shear rate and viscosity calculations

Probes	Volumetric rate of flow [cm ³ /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

Viscosity results and their analysis

Viscosity was determined according to the procedure described in 2.2.4. In Table 6 are given results of volumetric rate of flow, shear rate and viscosity calculations.

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

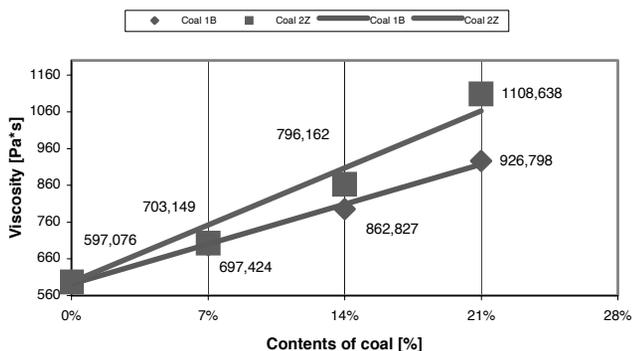


Fig. 5. Dependences of composites viscosities on hard coal contents

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.1 and Fig. 2). Linear character of observed dependences induced us to compare experimental results with that calculated according to Einstein's theory.

Einstein's equation (11) may be written as:

$$\eta_r = \frac{\eta}{\eta_0} = 1 + 2,5\phi \tag{23}$$

where:

η_r – relative viscosity of dispersion.

In the Table 7 are given results of relative viscosity calculations obtained from experimental results and according to Einstein's theory.

Table 7. Results of relative viscosity calculations

Composite	Experimental relative viscosity	Relative viscosity according to Einstein
PA	1.000	1.000
1B7%	1.168	1.154
1B14%	1.333	1.311
1B21%	1.552	1.471
2Z7%	1.178	1.152
2Z14%	1.445	1.307
2Z21%	1.857	1.465

Figure 6 and 7 show dependences of relative viscosities on filler contents obtained in experiments in comparison with results calculated according to Einstein's theory.

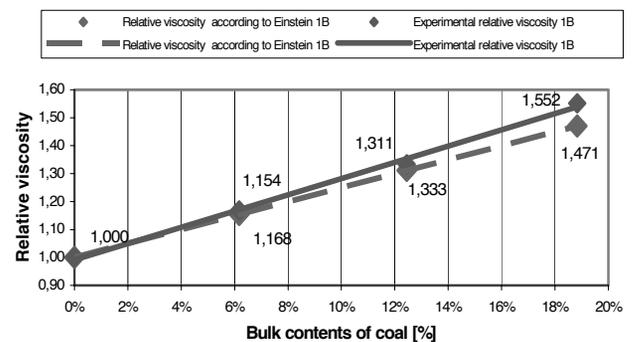


Fig. 6. Comparison of experimental and theoretical dependences of viscosity on filler content for 1B hard coal

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. Linear character of experimental dependences made it possible to modify Einstein's equation in to form being the first two terms of eq.(12) series:

$$\eta_r = \frac{\eta}{\eta_0} = \sum_{n=0}^{n=1} c_n \cdot \phi^n = c_0 + c_1 \cdot \phi \tag{24}$$

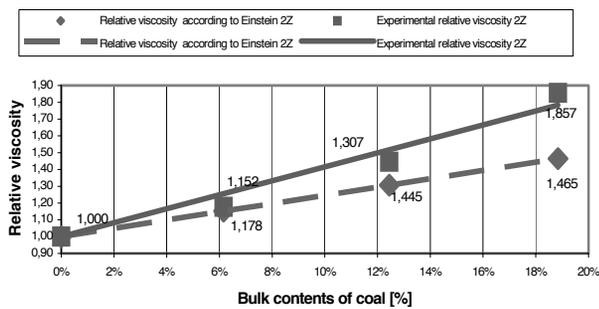


Fig. 7. Comparison of experimental and theoretical dependences of viscosity on filler content for 2Z hard coal

Fig. 6 and 7 show that ' c_0 ' may be taken as $c_0=1$. c_1 values for both coal types were calculated using least squares procedure of experimental results approximation with linear function. For composites with 1B hard coal particles $c_1=2.85$ And for 2Z hard coal particles $c_1=4.16$. Correlation coefficients were $r^2=0.99$ and $r^2=0.96$ respectively.

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 0.035mm.

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