

Hard coal modified with silanes as polyamide filler

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Properties

ABSTRACT

Purpose: This paper shows the influence of coupling agents, especially silanes, on mechanical properties of polyamide 6 filled with hard coal dust.

Design/methodology/approach: Before preparing compositions, pulverised filler surface was modified with coupling agents. Then, it was compounded using a twin-screw extruder composite consisting of modified hard coal and polyamide 6. A blend was granulated later and test samples were subjected to injection moulding. Afterwards, mechanical properties were evaluated. These properties have essential meaning for applications of new composites as structural materials.

Findings: Tests demonstrated that modification of powdered hard coal surface with coupling agents had not significant effect on mechanical properties of polyamide/hard coal composites.

Research limitations/implications: Applied compounding procedure did not allow to achieve good compositions homogenisation. A new method to be applied is planned in future research. Simultaneously, it is necessary to investigate composites with other coupling agents which will improve filler's adhesion to a polymer. Long-term test are also planned.

Practical implications: Hard coal, cheap and widely available filler, used to modify thermoplastic polymers, enable to obtain new materials with attractive properties and many applications.

Originality/value: Paper represents innovative polymer filler and methods to modify it.

Keywords: Polymers; Composites; Hard coal; Engineering materials; Strength tests

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1. Introduction

In the recent years, higher and higher requirements concerning structural materials have focused our studies on developing new materials and especially on modification of the existing ones. Polymer structural materials are more and more widely used in almost all industry branches of engineering practices. These materials offer many features that substantially differ from materials, such as metals, ceramics, or glasses, and simultaneously

their processing does not require high energy outlays. Properties of polymer structural materials are very well recognized but a possibility to create new composites with them makes producing modern materials of new properties possible [1, 2].

The easiest way to get different or new properties is to use fillers. Fillers are defined as solid particles introduced to polymeric matrix of weight fracture at least 10%. Presently, in commercial use there are fillers of polymer matrixes in a form of different fibres and dusts.

It is possible to distinguish two types of them: reinforcing or active fillers which improve mechanical and/or other properties of composites and passive fillers (extenders), the aim of them is to decrease material costs without decreasing the functional properties [3, 4, 5, 6].

It is worth saying that in highly filled composites a polymer plays a role only as a binder which couples filler particles together and in working conditions it transmits external loadings [7, 8].

In industrial practice it is possible to distinguish many types of powder fillers. The most common are mineral particles: kaolin, chalk and quartz flour, powdered mica, graphite, dolomite flour [9], and organic particles: ground fruit's stones, ground seeds, wood flour and many others. Influence of typical fillers on thermoplastic and thermosetting resins properties is not well known. Simultaneously, there are new fillers which influence on high molecular weight polymers and they are not known either. One of such fillers is pulverised hard coal [10, 11]. Therefore, in the recent years, The Institute of Engineering Materials and Biomaterials, Department of Metal and Polymer Materials Processing of The Silesian University of Technology carried out scientific research on applying hard coal particles as polymers modifier. Also, application of coupling agents as filler particles surface modifier was investigated. Research focuses on influence of percentage content, particles size and geometry on mechanical and processing properties of epoxy, polyethylene and polyamide composites. To utilize these engineering materials, it is required to possess extensive knowledge about their properties such as mechanical, rheological, electrical, magnetic, and thermodynamic properties. Simultaneously, one cannot expect that all the features will be improved. We have to admit that no ideal filler exists, whose versatile influence could substantially improve all polymer properties. In practice, improvements of one or a few properties are enforced by deterioration of the other [12].

It is indicated that the main unwanted effects of fillers application to modify polymeric matrixes are the following [13, 14]:

- appearance of composition homogeneity caused by sedimentation and particles aggregation,
- decrease of mechanical properties caused by agglomeration,
- deterioration of processing properties,
- enlarged absorption of moisture which affects deterioration of dielectric properties,
- decrease of mechanical properties caused by unsuitable adhesion between fillers surface and matrix.

Performance, and among them, the mechanical properties are the main criterion which decide about possible application of a newly formed composite as engineering material.

To achieve reinforcing effect of filler particles on polymeric matrix, many different factors have to be taken into consideration. Chemical structure of polymer and filler, shape and size of filler particles, particles size distribution, dispersion of solid particles in polymeric matrix, adhesion between solid particles and matrix, and morphology of complete composite system are the main factors determining the reinforcing effect. Also, the process of composite formation is very important. To achieve good adhesion molten polymer has to wet the surface of solid particles completely. It is determined mainly by surface energy of both components. Shear stresses during mixing process also play very important role in wetting stage of composite formation. The same stresses disintegrate particles agglomerates [15, 16, 17].

To improve or to create chemical and/or physical bonds between filler's particles surface and polymer matrix many a time coupling agents are applied.

Large group of fillers is characterised by surface of polar and hydrophilic character. Silica dioxide could be an example whose hydrophilic properties come from numerous silanol groups which undergo transformation into siloxane group in the temperature of about 200°C. As it is known, occurrence of considerable amount of water on filler's surface has negative influence on its wetting ability and dispersion in molten polymer. Dispersion of solid particles in polymer is one of the factors that decide about filler and polymer matrix bonds durability.

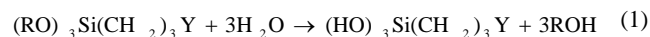
A possibility to use silanes as coupling agents comprises both thermosetting resins and thermoplastic polymer materials. Using the coupling agents for polymer – inorganic filler systems can improve mechanical properties but also electrical, water-repellent properties. The main advantage of their use is enhancement of long-term characteristics such as thermal stability, fatigue strength and ageing resistance. In a case of filler's surface, a modifying agent makes only appropriately strong bonds possible between polymer matrix and fillers surface to achieve favourable transfer by matrix of the stresses arising in time of composite exploitation. To connect components, for example, filler particles of large elasticity modulus and a polymer of small elasticity modulus, an intermediate layer of mean properties are necessary. This can be provided by adequately chosen surface wetting or coupling agent.

The main problem in the first stage of filler's surface modification research is to choose the coupling agent adequately. The group of the most widely used coupling agents from the commercial standpoint are silica-organic compounds. Those substances, popularly known as silanes, enable to change properties of solid particles surface mainly because they contain free hydroxide groups. The main coupling agents from that group of modifiers are presented in Table 1 [18].

Silica-organic coupling agents with general formula $(RO)_3Si(CH_2)_nY$ are characterised by two types of functional groups. RO substituent group is an easily hydrolysed alkoxy group, such as $-OCH_3$ or $-OC_2H_5$, and functional group $(CH_2)_nY$ is usually carbo-functional group. Methods of applications of silica-organic coupling agents comprise two basic procedures:

1. In the first method filler's surface is preliminary treated with coupling agents. Coupling agent can appear in a form of water solution, solution in organic solvent or without solvent – a pure coupling agent only.
2. In the second method silane coupling agent is introduced directly into molten polymer before or after mineral filler addition.

Water as diluent causes hydrolyse of alkoxy group and gives silanetriol according to reaction shown in the following equation (1):



In case of glass surface for example glass fibres, process of silane adsorption will take no more than 30 seconds. Then, condensation of silanol group proceeds on silica dioxide surface (SG-OH) with one of hydroxide group of silanetriol $(HO)_3Si(CH_2)_3Y$. As an effect of reaction, it precedes formation of siloxane bond which is shown in the following reaction equation (2):



In organic solution condensation proceeds between silanol group which is on silica dioxide surface and alkoxy group of silane. Formula of this reaction is shown in reaction equation (3):



Table 1.
Characteristics of silane coupling agents

Chemical formula	$(\text{CH}_3\text{COO})_3\text{SiCH}=\text{CH}_2$
Name of a chemical compound	Vinyltrimethoxysilane
Manufacturer ¹⁾	UCC, DC, CHISSO, W
Chemical formula	$(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{OCOC}(\text{CH}_3)=\text{CH}_2$
Name of a chemical compound	3-(trimethoxysilyl)propyl methacrylate
Manufacturer ¹⁾	UCC, DC
Chemical formula	$(\text{C}_2\text{H}_5\text{O})_3\text{SiCH}_2\text{CH}_2\text{SH}$
Name of a chemical compound	2-Merkaptoethylotrietoxy-silane
Manufacturer ¹⁾	UCC
Chemical formula	$(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{SH}$
Name of a chemical compound	Merkaptopropyl trimetoxysilane
Manufacturer ¹⁾	UCC, DC, CHISSO, GE, W
Chemical formula	$(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{Cl}$
Name of a chemical compound	chloropropyltrimethoxysilane
Manufacturer ¹⁾	UCC, DC, CHISSO, W
Chemical formula	$(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$
Name of a chemical compound	3-aminopropyltriethoxysilane
Manufacturer ¹⁾	UCC, CHISSO, GE

¹⁾ UCC – „Union Carbide Corp.“, USA; DC – „Dow Corning Corp.“, USA; CHISSO – „CHISSO Corp., SP Division“, Japan; GE – „General Electric Corp.“, USA; W – Wacker-Chemie GmbH., Germany

Process of bonding the silane preparation with glass surface proceed as functioning hydroxides ions OH⁻ coming from adsorbed surface water layer. These agents provide covered glass fibres surface with water repellent properties. In the effect moisture-resistance and resistance to atmospheric influences is formed. Introduction of vinyl radical into silica-organic coupling agent, chemical structure makes their copolymerisation with polyesters vinyl radical possible, the main types of resins applied by these surface modifiers [18].

Simultaneously, in case of mineral fillers it is possible to observe their diversified behaviour in relation to silane coupling agents. Strengthening influence of coupling agents is especially effective in composites including fillers which surface is of neutral or alkali character such as silica, glass, aluminium oxide. At the same time, in case of alkali surface, those fillers as magnesium carbonate (magnesite powder), calcium carbonate, or

carbon black are distinguished by low effectiveness. Essentially, a better effect for this kind of fillers can be obtained using titanium or zirconium coupling agents. [19].

2. Experimental

2.1. Materials

In the present research programme the following materials are used:

- Polyamid 6 of the trade name „Nevimid 6 MLD Naturale“ manufactured by „Nevicolor“ (Italy).
- Coal filler in pulverised form: hard coal type 35, coming from The Zofiówka coal mine, milled and sieved with a sieve mesh diameter 0.035 [mm].

Physical properties and chemical constitution of hard coal used as dust filler of polyamide 6 is shown in Table 2

Table 2.
Hard coal physical and chemical properties

Hard coal type 35	
Density [g/cm ³]	1.33
Chemical constitution [weight fracture - %]	
C	88.46
H	4.68
O	4.46
N	1.87
S	0.52

To modify the hard coal surface, the following silica-organic coupling agents produced by GE Advanced Materials-Silicones, USA are used:

- Silan A-1100 (chemical structure: gamma-aminopropyltriethoxysilane);
- Silan A-172E (chemical structure: vinyl tri(2methoxyethoxy)silane);
- Silan A-174NT (chemical structure: gamma-methacryloxypropyltrimethoxysilane).

In Tables 3, 4, 5 physicochemical properties of the above-mentioned coupling agents are presented.

Table 3.
Physicochemical properties of silane A1100 [20]

Form	liquid
Colour	pure
Smell	amines
Melting point	< -70°C
Boiling point/range	220 °C in 1013hPa
Flash point	96 °C Method: ASTM D 93
Vapour pressure	< 1.33 hPa in 20 °C
Density	0.95 g/cm ³ in 25 °C (1013 hPa)
Solubility in water	Reacts fast

Table 4.

Physicochemical properties of silane A-172E [21]

Form	liquid
Colour	pure
Smell	ester
Melting point	< -70°C
Boiling point/range	285 °C in 1013hPa
Flash point	92 °C Method: ASTM D 56
Vapour pressure	< 6.65 hPa in 20 °C
Density	1.04 g/cm ³ in 25 °C (1013 hPa)
Solubility in water	Reacts slowly

Table 5.

Physicochemical properties of silane A-174NT [22]

Form	liquid
Colour	pure
Smell	ester
Melting point	< -40°C
Boiling point/range	255 °C in 1013hPa
Flash point	108 °C Method: ASTM D 56
Vapour pressure	>1
Density	1.045 g/cm ³ in 25 °C (1013 hPa)
Solubility in water	Reacts slowly

2.2. Samples preparation

Hard coal used for research filler in a pulverised form was prepared in the following way. Purchased raw material, pea coal, had a mean particle diameter of about 50 mm. To enable successful milling, pea coal was dried in an oven with air circulation in the temperature of 105°C for 24 hours. This allowed reducing coal humidity below 2%. Then, coal particles were crushed and milled in following devices:

- alligator crusher,
- beater mill,
- ball mill (Fig. 1).

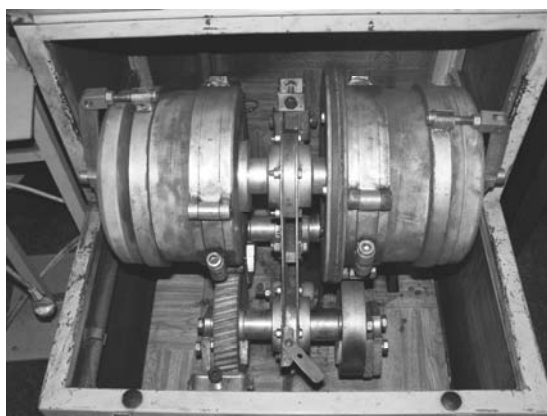


Fig. 1. The ball mill used in filler preparation

Crucial for achieving the final particle size was to process it in a ball mill. One milling process gave 0.5 kg filler particles. Before milling, this portion of coal was put together with 4 kg of milling balls into a milling chamber. The milling time of one portion was 15 minutes. Afterwards, the pulverised coal was sieved on a sieve mesh diameter 0.035 [mm]. It allowed excluding particles of bigger diameter. Ready filler was stored in leakproof containers to avoid humidity uptake.

In the next step, in order to obtain filler with suitable properties of surface, a part of prepared hard coal filler was coated with silanes. The main purpose of this process was to enhance polymer macromolecules adhesion to filler particles surface.

As it was mentioned before, three types of silicorganic coupling agents were used. From among earlier presented methods of silanes application, water solutions coating was chosen. According to silane manufacturer, water with defined pH should be applied. This water reaction was different for different silanes. Demineralised water without any pH modification was used to dissolve A 1100 silane. For the rest of silanes pH was modified with 35% hydrochloric acid (HCl). For A-172E solvent, needed pH was 4, 5-5 and it was obtained adding 150 ml of hydrochloric acid to one litre of demineralised water. For A-174NT it was necessary to apply water with pH value of 3.5-4 and it was obtained by 185 ml acid addition to one litre of demineralised water.

In this way the prepared aqueous solutions, silanes were added. In 100 weight parts of water, one weight part of silane was dissolved. As result of the solvent mixing with silica-organic coupling agents, hydrolysis of alkoxy groups in silane molecules took place.

Filler dust was mixed up with silane aqueous solution. Coating process proceeded for about 45 minutes. After coating, in order to eliminate humidity, mixture was desiccated in the temperature of 85°C for 24 hours.

Afterwards, polymer-coal composites were prepared. Modified and unmodified hard coal was used as filler. First appropriate coal portions were weighted using laboratory analytical scales with the accuracy of 0.001 g. 7%, 14% and 21% contents were planned by weight. Next suitable portions of polyamide 6 were weighted (about 200 g). Polyamide was compounded with coated hard coal particles using a laboratory twin-screw extruder. Extruding die with diameter 3 mm was applied. Extrusion process was realised with the following parameters: temperature of the extruder zones 221-240°C, extruder screw rotation 6 r/min. Extruded composite rods were granulated later by granulator knives. Received granulated composite is shown in Figure 2. Compounding was performed in Laboratory of The Institute for Engineering of Polymer Materials and Dyes in Gliwice. Composites samples with total mass minimum 2.5 kg were extruded and granulated. Ready granulates were injection moulding compound to manufacture test pieces for mechanical tests.

The normal practice with polyamide is to be dried before injection moulding to remove moisture and to avoid probable defects of moulded parts, especially voids and sinks. Polyamide and its composites with coal, used in the research, were dried in laboratory drier with air circulation in the temperature of 80°C within 24 hours.

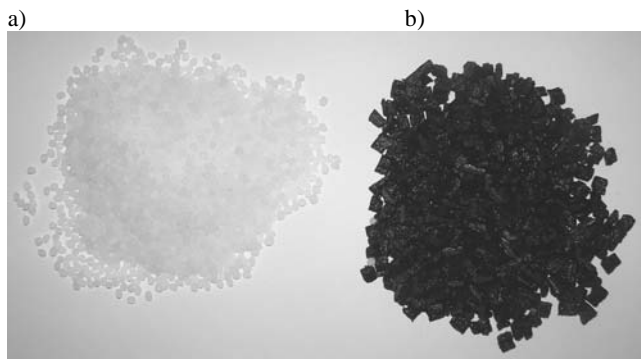


Fig. 2. Granulated composites used in injection process to produce test bars for mechanical tests; a) pure PA 6, b) PA 6 modified with hard coal

Dumbbell shaped test pieces were injected using Krauss Maffei KM65 160 C1 injection moulding machine. The following processing parameters were used:

- mould temperature - 60 [°C],
- injection rate - 25 [cm³/s],
- injection pressure - 70 [MPa],
- change-over time - 0,3 [s],
- holding time - 26 [s],
- zones temperature - 40-255 [°C].

After injection moulding test samples were subjected to accelerate conditioning in water in the temperature of 70°C for 8 hours. In the second stage of conditioning the samples located for 2 weeks in a hermetic container.

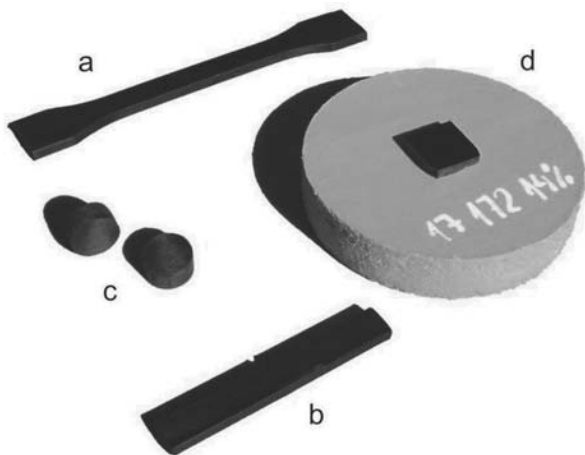


Fig. 3. Test pieces used in the research programme: a) dumbbell test piece for static tensile test, b) notched test piece for the impact test, c) test piece for abrasion resistance determination, d) test piece for the coefficient of friction determination

Dumbbell samples used in research are shown in Figure 3a. After conditioning, the samples were subjected to a static tensile test. The same test pieces were used to prepare the rest of test samples for the other mechanical tests.

Test pieces for impact strength tests, shown in Figure 3b, were prepared by machining. First, rectangular bars were cut and, in the next step, notches were milled with a special profile cutter with the angle 45° and radius of the notch base 0.25 mm. Test pieces applied for wear resistance measurements were cut using a pin-cutting drill of the internal hole diameter 16 mm (Fig. 3c). Because one disk cut in this manner was too thin, in order to provide suitable thickness, two discs were glued together, what is allowed by the Polish and European Standard PN-ISO 4649:2007.

To determine a coefficient of friction, using a method developed by The Central Mining Institute in Katowice, tests pieces were made with cuboids' shape. In order to place them in a testing device, test pieces were fixed to adhesive circular plates with diameter 100 mm and thickness 20 mm (Fig. 3d).

2.3. Testing procedures

Particle size analysis

Particle size distribution is one of the main characteristics defining pulverised fillers properties. In this preliminary stage of research, a sieve analysis was applied to evaluate pulverised hard coal particle size distribution. The analysis was performed using vibratory sieve particle size analyser. Sieves of mesh diameter from 0.1 to 0.035 mm were used.

Static tensile test

Tensile tests to evaluate strength characteristics were carried out using a universal tensile machine FPZ-100/1 (Heckert-Germany). The measurements were performed in accordance with the European and Polish Standard PN EN ISO 527-1. Tests were performed in the following conditions:

- tensile speed 50 mm/min,
- force range 4 kN,
- temperature 22 ± 2 °C.

Impact strength

The next performed test was the impact strength. Tests were realized by means of a notched Charpy method. The applied device was equipped with interchangeably working hammers of maximum impact energy equal to 7.5, 15, 25 and 50 J. Impact measurements were carried out in accordance with the European and Polish Standard PN-EN ISO 179-1:2000. The used device allowed for direct reading of energy absorbed to break the sample. These measurements were carried out in the following conditions:

- nominal energy of pendulum 7.5 J,
- angle of fall of the pendulum 160°,
- ambient temperature 23±1°C.

Samples of the type A notch were broken at the edge of impact mode.

Abrasion resistance

The purpose of these measurements that was to determine the effect of filler content and to use coupling agents on obtained composite attrition. The study was realized in a Schopper-Schlobach-type device. Measurements were carried out in accordance with the European and Polish Standard PN-ISO 4649:2007. Sample weight loss was taken as a measure of abrasion. Abrasion tests were performed in the following conditions:

- temperature $24\pm 1^\circ\text{C}$,
- abrasive cloth no. 60,
- force pressing the sample to abrasive cloth 10 N,
- distance travelled by the sample 40 m.

Coefficient of friction

Determination of the coefficient of friction was carried out using WTP/1 device. The device was designed and constructed, and the procedure was elaborated in The Central Mining Institute in Katowice. Measurements were performed in the following conditions:

- temperature $20\pm 1^\circ\text{C}$,
- base material- St3steel plate,
- force on the sample 20N.

3. Results and discussion

The results of the sieve analysis of particle size distribution are presented in Table 6 and in a form of bar diagram in Figure 4.

Table 6.
Particle size distribution of pulverised coal [4]

Charging material	Particle size [mm]	Content by weight [%]	Total content by weight* [%]
Coal	>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

* - This value gives a sum of weight content of particles with the size in a given range and smaller

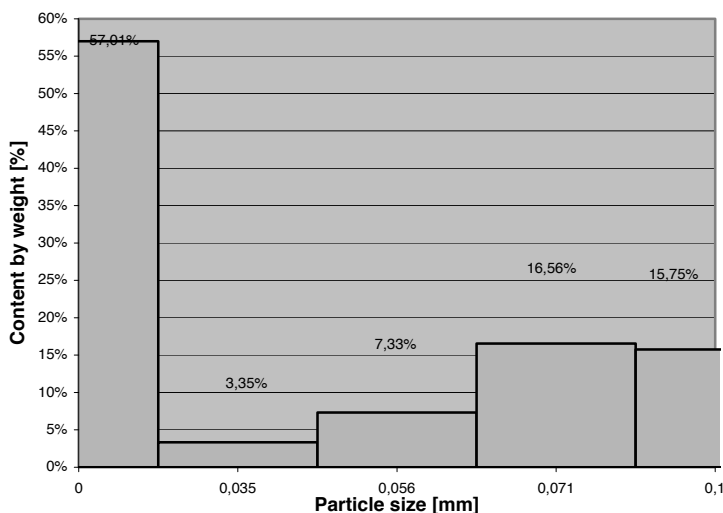


Fig. 4. Particle size distribution of coal filler dust [4]

As it is clear from the sieve analysis, the largest percentage in resulting dust filler had particles with the size less than 0.035 mm. To determine particle size distribution in the range 0 – 0.035 mm, the more precise tests are planned in near future.

3.1. Static tensile test results

Tensile tests were performed to determine two basic strength and deformation characteristics: tensile strength and elongation at break. In the paper all results are presented in a graphic form. Five measurements were made in every experimental point. Only mean values are shown. In addition, the results have been extended by results of analogues research of PA6 filled with unmodified hard coal from The Zofiówka and The Bolesław Śmiały Mine [23]. Figure 5 shows the modifier effect used for filling on tensile strength. In this and next figures the following abbreviations are applied:

- PA6 – virgin polyamide,
- PA6 + Zofiówka – polyamide with hard coal tested in this research,
- PA6 + Bolesław – results according to [23].

The effect of carbon content and a type of coupling agent on elongation at break and on elongation at maximum tensile force are illustrated in Figures 6 and 7.

Presented results show that compared to virgin polyamide 6 resin filler content has effect mainly on reduction of all tested properties. Fig. 5 gives evidence that tensile strength decrease almost linearly with increase of hard coal content. Also, deformation ability of polyamide 6 is reduced by searched filler. This is clear from the analysis of the results shown in Figures 6 and 7. Presented results also indicate that the applied organosilicon coupling agents have led to a decrease in tensile strength and relative elongation. This demonstrates that suitable coupling layer between filler and polymer, which should connect filler surface and matrix, was not created.

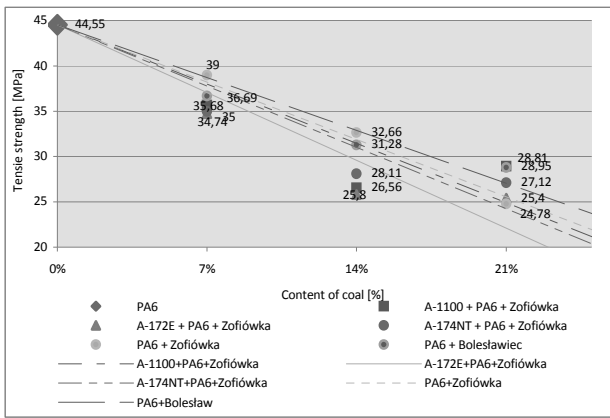


Fig. 5. Effect on content of a filler and a type of silane on the tensile strength

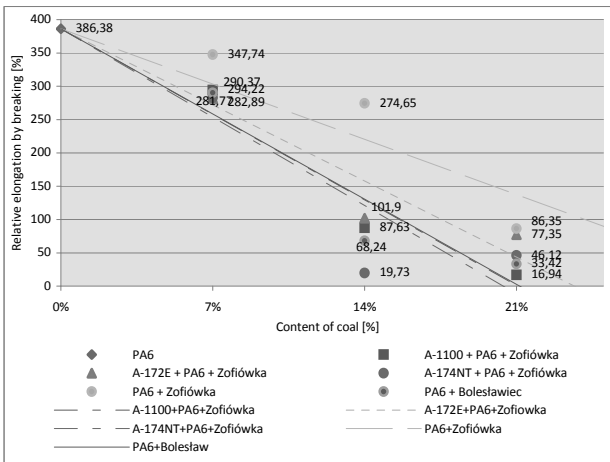


Fig. 6. Influence of carbon content and a type of silane on elongation on break

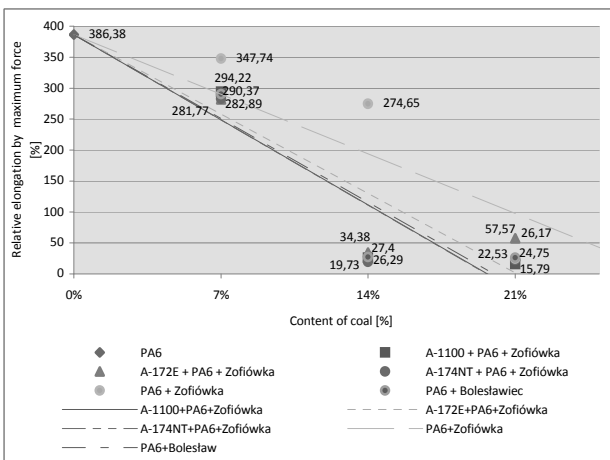


Fig. 7. Influence of carbon content and a type of silane on elongation at maximum force

3.2. Toughness results

Figure 8 summarizes the results of impact strength tests. Presented points show average values calculated from 5 measurements. Once more the presented analysis was extended with impact strength value for non-modified coals [23].

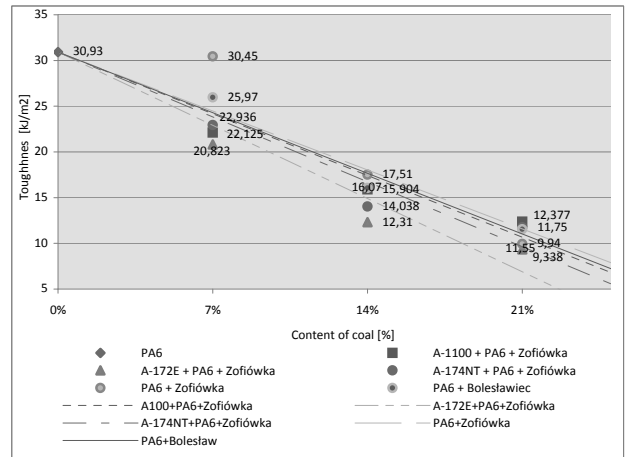


Fig. 8. Effect of filler content and silane type on toughness

As it can be seen on Figure 8 with increased coal content in composite values of toughness, it is decreased. Decrease in value is proportional and is about 8 J/m² for the filling of 7% and 14%. By contrast, for coal content of 21% the decrease is about 3 J/m². We can also find that there is influence used coupling agent for analyzed parameter. The lowest value for measuring property in all range of filling has silane A-172E.

Taking into account the tensile strength and impact strength results, hard coal may be used as an extender, lowering resin price but in the same time deteriorating the strength properties.

3.3. Abrasion resistance

Average values obtained in abrasion resistance tests are shown in Figure 9.

Analysis of results presented in this figure proves that also abrasion resistance is decreased as an effect of hard coal content in polyamide 6. The lowest mass loss was observed for a composite with modified hard coal by silane A-172E. It is interesting that for compositions modified by silane A-1100 and A-174NT by filler content 14% values of sample weight loss were lower than for compositions with 7% filler content. It indicates that for these composites higher addition of coal may increase the abrasion resistance. To verify observed tendency, additional research is needed.

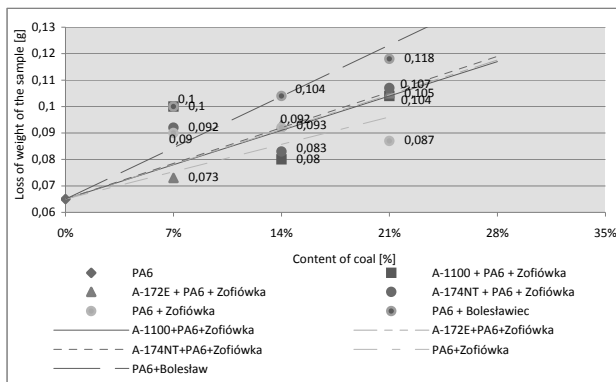


Fig. 9. Influence of filler content and a type of silane on average sample weight loss in abrasion test

3.4. Coefficient of friction

Result of the coefficient of friction investigations are presented graphically in Figure 10.

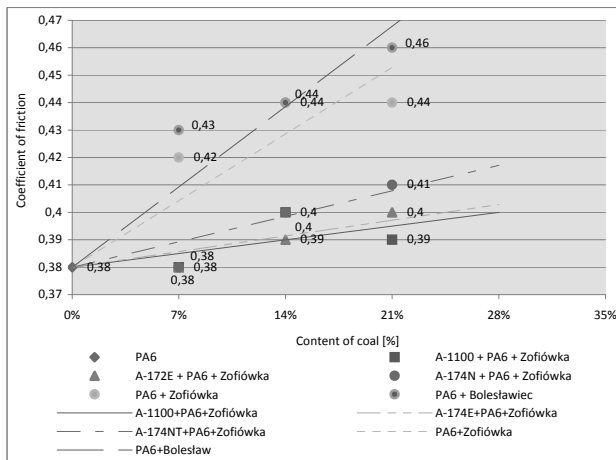


Fig. 10. Influence of filler content and a type of silane on coefficient of friction

Results confirm generally observed increase of coefficient of friction as a result of hard filler incorporation. More interesting is that presence of coupling agents has effect on decrease of coefficient of friction in comparison to unmodified fillers. This tendency is observed in all ranges of filler content. It can also be observed that coefficient of friction increase along with increasing filler content is lower when hard coal particles are modified by silane. Summarizing the coefficient of friction results, it can be said that silane coupling agents reduce this coefficient.

4. Conclusions

- (1) Hard coal particles with and without silane coating caused strength properties decrease. Hard coal may be used as an extender, lowering resin price.
- (2) Silane coupling agent did not form strong adhesive bonds between polyamide matrix and hard coal particles.
- (3) Silane coupling agents caused decrease of coefficient of friction of searched composites.
- (4) Additional research is needed and planned on the other coupling agent capable to form strong adhesive bonds between filler and polymeric matrix. In the following research titanates, zirconates and organic-chromium chromium chloride coordination complex will be tested.

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