



Research on polyamide matrix composites filled with hard coal

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ABSTRACT

Purpose: The aim of this paper is to present the summary results of studies on polyamide composites filled with hard coal. Research on the use of coal as a filler of polymers are conducted for many years in Division of Metallic and Polymeric Materials Processing, Silesian University of Technology. This paper summarizes results obtained in different research programmes performed in recent years. Described materials are polyamide 6 composites filled with modified and unmodified hard coal powder.

Design/methodology/approach: All the resulting compositions intended for research have been produced using twin screw extruder. The resulting mixtures of various compositions were then subjected to a process of granulation. The prepared composites have undergone a process of injection moulding which allowed to obtain samples for strength tests. Full statement of research results obtained for composites could help to predict the material with the best mechanical properties and hence the best material for construction.

Findings: It has appeared from studies that in both a composite made of unmodified coal and of coal modified with coupling agents show a decrease in mechanical properties in comparison with the neat polymer. Apart from this these composites are interesting materials because of low price of the filler.

Research limitations/implications: It can be concluded from research that all types of obtained composites are characterized by a decrease in mechanical properties.

Practical implications: Applications of hard coal as a filler of polymer composites is way to produce new materials. It is worth noting that the main features of the filler used is its prevalence, low cost and electrical conductance.

Originality/value: The results describe new fillers of thermoplastic polymers and the possibility of its modification.

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

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MATERIALS

1. Introduction

Demands posed by current technique for engineering materials force to search for new materials or changing the properties of existing materials that will meet desired requirements. Engineering polymeric materials have found a permanent place in technical practice as materials that are commonly used in all industries. These materials offered a wide range of very different properties, substituting materials such as ceramics, glasses and metals. Low levels of investment in the processing of polymers have made the materials very prevalent in everyday life. It is worth to noting that engineering polymer composites have been known very well to date. However possibility of producing new composites based on old engineering materials gives us a big hopes to make new materials with innovative properties [1, 2].

It is necessary to cope with the increasingly demands to modern materials. It is the main reason that the Institute of Engineering Materials and Biomaterials, Department of Metal Processing and Polymer Materials, Silesian University of Technology for many years is involved in research on the use both unmodified and modified hard coal as a filler in polymeric materials.

Willingness to use the newly created composite as universal engineering materials need to know not only its mechanical properties and processing but also magnetic, electrical and thermodynamic properties. At the same time, strength characteristics are the main factor determining the use of the newly formed material in today's technology. The use of fillers is the easiest way to modify and achieve different or new features in the case of polymeric materials. In principle it is possible to specify the two main types of fillers [3-6]:

- Active fillers – the aim of those is improving strength properties in obtained composites,
- Passive fillers – their main purpose is to reduce the manufacturing cost of composites without significantly reducing its characteristics.

The most common fillers used for producing polymer matrix composites are various forms of fibres and powders. As filler we call solid particles in the polymer of which content is approximately 10% by the weight. An important feature of highly filled polymer composites is the fact that the polymer matrix acts as a binder whose task is to combine the fibres or particles of filler [7, 8].

As indicated in industrial practice it is possible to specify a large amount of used powder fillers. The most commonly used are [9]:

- kaolin,
- powdered chalk and precipitated calcium carbonate,
- powdered quartz,
- mica,
- graphite,
- dolomite flour,
- talc.

The fillers and their influence on the properties of both thermoplastics and thermosetting resins has been understood in detail, so they may be called typical. At the same time it is possible to apply the new fillers such as hard coals whose impact on the properties of plastics is not yet fully understood [10].

Very important is the fact that it is not possible to obtain a significant improvement of all listed properties. It should be pointed that it is not possible to obtain an ideal filler that effects on polymer which would be versatile enough that contributed significantly to the improvement of all the known properties. The actual improvement in one or more of the properties is burdened with worsening many others [11, 25].

The most commonly found negative effects occurring during the use of fillers are [12, 13, 25]:

- sedimentation leading to the formation of inhomogeneities,
- agglomeration resulting in a reduction of strength,
- difficulty to obtain appropriate processing properties,
- reduction of dielectric properties due to the presence of increased absorption of moisture,
- significant deterioration of mechanical properties due to improper surface characteristics.

The process of creating polymer reinforcing by the fillers depending on many factors. Among the most important conditions affecting the change of properties of the composite can be distinguished: chemical structure of polymer and filler, the kind of phase, size and shape of the filler particles, area of distribution of dispersed and diffuse phase, processing conditions and in particular the mixing of ingredients and the process of forming composites, and one of the most important factors is occurrence of adhesion of polymer matrix to the filler particles. Not without a significance is the fact that the possibility of proper wetting of the filler by the polymer matrix determines the correct mixing process which results in adhesion between polymer matrix and the filler, and obtaining the effect of reinforcement [14].

Fillers with polar or hydrophilic surface nature are major groups among these materials. A typical example of the filler belonging to this family is the hydrophilic silica obtained by the presence of many silane groups, which due to the thermal effect around 200°C are converted to siloxane. An important element often determining the possibility of a proper connection of the filler and the matrix are the properties of dispersion. Process of dispersion and wetting of the filler surface by the polymer is often disturbed by the presence on the filler surface large quantities of water whose presence is highly undesirable [15, 16].

Application of coupling agents in the polymer-filler system is the main method of producing or improving physical or chemical connections in this system.

Commonly used adhesion promoters both silanes and titanates have a wide field of applications for both modified thermosetting resins and thermoplastics. In order to improve mechanical and electrical properties, thermal stability of hydrophobic or finished products the use of coupling agents in polymer-filler system could bring many benefits. At the same time it is worth noting that in the case of modifications of filler surface only sufficiently strong connection with the polymer matrix may allow the occurrence of positive transfer of stresses that affect the composite during its normal use. Frequently occurring problem is the need to combine two very different systems. An example is a filler with very high modulus and a polymer with a small modulus. The solution in this case is formation an interlayer between two different materials with intermediate properties. All of these features can provide only properly chosen aperture. The basic problem is the correct choice of the coupling agent during attempts to modify the surface of the fillers. One of the most commonly used coupling agents are organosilicon and are titanate adhesion promoters.

The main feature of the substance commonly called silanes is the possibility of impact to change properties in surface of solids containing free hydroxyl groups. Among the coupling agents is possible to enumerate the most widely used. These include [17, 25].

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

- $(\text{CH}_3\text{COO})_3\text{SiCH}=\text{CH}_2$, Vinyltrimethoxysilane, UCC, DC, CHISSO, W,
- $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{OCOC}(\text{CH}_3)=\text{CH}_2$, 3-3-(trimethoxysilyl)propyl methacrylate, UCC, DC,
- $(\text{C}_2\text{H}_5\text{O})_3\text{SiCH}_2\text{CH}_2\text{SH}$, 2-Merkaptoethyltriethoxy-silane, UCC,
- $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{SH}$, 3-Merkaptopropyl trimethoxysilane, UCC, DC, CHISSO, GE, W,
- $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{Cl}$, 3-chloropropyltrimethoxysilane, UCC, DC, CHISSO, W,
- $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$, 3-aminopropyltriethoxysilane, UCC, CHISSO, GE.

1.1. Characteristics of organosilicon coupling agents

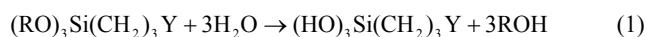
Basic adhesion promoters such as organosilicon coupling agents are characterized by the presence of two types of functional groups. General formula of this substances is $(\text{RO})_3\text{Si}(\text{CH}_2)_n\text{Y}$. There are some substituents possible to distinguish:

- RO – is a substituent of alkoxy group (OCH_3 lub OC_2H_5) which hydrolyze easily,
- $(\text{CH}_2)_n\text{Y}$ – is a substituent of carboxyfunctional group.

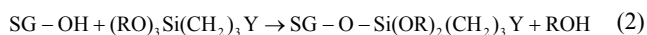
Among organosilicon coupling agents two methods of application can be basically distinguished:

- In the first method the adhesion promoter is applied as an aqueous solution, the solution in an organic solvent or in pure form. Filler surface is subjected to pre-treatment by adhesion promoter;
- The second method involves mixing a coupling agent with both the filler and the polymer.

Using water as a solvent results in the hydrolysis and forming a silanetriol, what is shown by the reaction model (1).

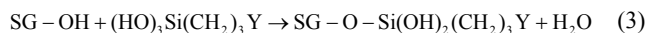


However, in the case of the use of silane solutions with organic solvents condensation occurs between the silane group present on the surface of silica and alkoxy group of silane. The reaction illustrates the scheme of reaction (2):



For the most typical filler which is fibreglass bonding process of silane with the surface of the filler occurs through the presence of OH ions. These ions originate from layer of water adsorbed on the glass surface. The process of adsorption on the surface of glass fibre is terminated after about 30 seconds. And then there is

a condensation of silanol groups of silica surface with one hydroxyl group of silanetriol. This leads to the formation of siloxane bonds presented by a model (3).



The use of these measures provides the coated glass surface hydrophobicity resulting in good resistance to water and weather conditions. At the same time the primary determinant of the widespread use of such preparation is the presence of vinyl radical in the molecule of organic silicon which allows for copolymerization with polyesters [17].

It is worth noting that the different silane promoters behaviour was observed in relation to different mineral fillers. High efficiency of this type of adhesion promoter was observed for composites whose fillers exhibited surface properties of a neutral or alkaline nature, in particular alumina, silica and glass. It should be noted that for fillers such as magnesite, calcium carbonate and carbon black which surfaces are basic in nature these coupling agents are not performing well. Achievement of better outcomes are possible through the use of zirconian or titanium adhesion promoters [18, 25].

1.2. Characteristics of titanate coupling agents

Coupling agents such as titanates essentially perform similar function as previously described organosilicon materials. Among the main features which characterize these filler-polymer system are: improving the adhesion, strengthening the catalytic reaction, improving the filler dispersion and improving the rheological properties of the composite. In many cases the use of titanates allows for a significant increase of filling degree of compositions with inorganic fillers [19]. The main advantages of using titanium coupling agents in manufacturing processes and in exploitation are [19, 24]:

- Durability of parts is increasing,
- The dosage is made directly to the mixture,
- Coupling agents are used in small amounts from 0.2 to 1%,
- Increasing is the corrosion resistance,
- Reduced is the viscosity of the composite mixtures and thereby improved is the flow of material.

2. Materials for research

For preparing carbon-polymer composites for tensile test the following materials were used [24, 25]:

- Polyamide 6 with trade name „Nevimid 6 MLD Naturale” produced by „Nevicolor”;
- Hard coal powder filler: hard coal type 35 from Zofiówka mine, milled and sieved by sieve with 0.035 [mm] mesh diameter.

At the same time some of composition contain a hard coal filler with modified surface. For surface modification the following organosilicone and titanate coupling agent were used:

- Silan A-1100 with chemical name aminopropyltriethoxy-silane.

- Silan A-172E with chemical name vinyl tris(2-methoxyethoxy)silane.
- Silan A-174NT with chemical name gamma-metacryloxy-propylotrimetoksysilane.
- Titanate KR 12/H with content: 65% KR 12/H ((*Tris (dioctylphosphato-O'')(propan-2-olato)titan*) and 35% silicon dioxide
- Titanate KR TTS/H with content: 65% KR TT S/H ((Titan-IV 2-propanolato, tris(isooctadecanoato-O-)) and 35% silicon dioxide.

Coupling agents used in research are manufactured by: titanates „Ken-React” whilst silanes „GE Advanced Materials-Silicones”.

Table 1 contains the summary of physical properties and chemical composition of hard coal filler. Whilst in Tables 2, 3, 4, 5, 6 the main properties of adhesion promoters are shown.

Table 1.
Physical properties and chemical composition of hard coal filler

Hard coal type 35 from Zofiówka mine	
Density, g/cm ³	1.33
Element content, % wt.	
C	88.46
H	4.68
O	4.46
N	1.87
S	0.52

Table 2.
Physicochemical properties of silan A-1100 [19]

Physical form	liquid
Colour	clear
Smell	amine
Melting point	< -70°C
Boiling point	220°C in 1013 hPa 96°C Method: ASTM D 93
Vapor pressure	< 1.33 hPa in 20°C
Density	0.95 g/cm ³ in 25°C (1013 hPa)
Water solubility	Reacts fast

Table 3.
Physicochemical properties of silane A-172E [20]

Physical form	liquid
Colour	clear
Smell	esther
Melting point	< -70°C
Boiling point	285°C in 1013 hPa
Flash point	92°C Method: ASTM D 56
Vapor pressure	< 6.65 hPa in 20°C
Density	1.04 g/cm ³ in 25°C (1013 hPa)
Water solubility	Reacts slowly

Table 4.
Physicochemical properties of silane A-174NT [21]

Physical form	liquid
Colour	clear
Smell	esther
Melting point	< -40°C
Boiling point	255°C in 1013 hPa
Flash point	108°C Method: ASTM D 56
Relative vapor density	>1
Density	1.045 g/cm ³ in 25°C (1013 hPa)
Water solubility	Reacts slowly

Table 5.
Physicochemical properties titanate KR 12/H [24]

Physical form	Solid powder
Colour	Light yellow
Smell	charakterictic
Melting point	-
Boiling point	71°C in 1013 hPa
Flash point	148°C Method: ASTM D 56
Relative vapor density	>1
Density	-
Water solubility	Non soluble

Table 6.
Physicochemical properties of tytanate KR TTS/H [24]

Physical form	Solid powder
Colour	white
Smell	Fat
Melting point	-
Boiling point	148°C in 1013 hPa
Flash point	93°C Method: ASTM D 56
Relative vapor density	-
Density	0.950 g/cm ³ in 25°C (1013 hPa)
Water solubility	10 g/l

Filler used in the studies in the form of pulverized coal has been obtained as follows. Purchased raw material was in the form of pea coal with grain size about 50 mm. Decreasing of grain size was obtained by mechanical treatment. Mechanical treatment of coal was carried on the following devices:

- Alligator crusher,
- Beater mill,
- Ball mill.

After primary mechanical treatment the material was pulverized with ball mill. It is worth to saying that the humidity of milled material was below 2%. Milling in ball mill had a basic importance on obtained grain size. Milling process was carried with following parameters: during milling one portion of filler in milling chamber of ball mill was 0.5 kg and 4 kg of balls were added, while milling time was chosen experimentally and was about 15 minutes. Figure 1 illustrates ball mill applied for acquirement of the filler.

For obtaining filler with relevant properties modification of filler surface was carried. The aim of modification was relevant

covering of filler surface with coupling agents. As it was said, covering of powder filler with organosilicon or titanate coupling agent have to improve adhesion between filler and polymer matrix. For modification 3 silane coupling agents and 2 titanates were used. Titanates were added directly to polymer-filler mixture in aim to introducing it in form of powder. Titanate coupling agent in both cases was added in content of 1% by weight. Modification by silane was carried by aqueous solution of silane method. Aqueous solution of silane was prepared as follow: as a solvent demineralised water was used. It is worth to note that these silanes should be prepared with water with relevant pH. Relevant pH was obtain by using 35% solution of hydrochloric acid. The pH value varied depending on the used organosilicon coupling agent. Methodology of preparing solvent with accurate pH value is shown below:

- pH of silane A-172E with solvent was 4.5-5. The value was obtained by adding 150 µl of hydrochloric acid to 1 L of demineralised water,
- pH of silane A-174NT with solvent was 3.5-4. The value was obtained by adding 185 µl of hydrochloric acid to 1 L of demineralised water,
- there was no necessity for pH correction of silane A-1100.

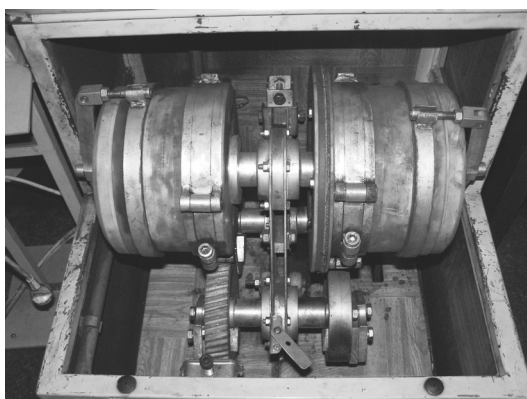


Fig. 1. Ball mill with drive gear [25]

Relevant modification of solvent allow for preparing good mixture of mineralized water and organosilicon coupling agents. The amount of silane dosing in all cases was one part by weight per hundred parts by weight of solvent. Mixing the silane with properly prepared portions of the solvent led to the hydrolysis reaction of alkoxy groups in the molecules of organosilicon coupling agents.

Powder filler was covered by suitable prepared solutions of silane. Next step was removing of water from the mixture what was achieved by filler drying.

In order to produce a composite for all used coupling agents 200 g weighed sample were prepared. The compositions were prepared in three weight ratios of 7%, 14%, 21%. All prepared weighed sample was performed on a laboratory analytical balance. The prepared feed material was subjected to an extrusion in laboratory twin screw extruder "Leistritz". The prepared composite was then granulated by a knives granulator. The prepared pellets were then used to prepare samples for strength tests. These samples were produced in the method of injection moulding. Injection of samples was performed with the ARBURG

injection moulding machine. The process of extrusion and injection of samples was conducted in the Central Mining Institute in the Department of Materials Science and Engineering [24, 25].

3. Description of achieved results of research

Before strength test of composite the sieve analysis of filler was carried out, directly after milling process of filler and before modification of filler surface. Sieve analysis was performed to estimate the particle size distribution. With the obtained results it is possible to determine their percentage in the resulting composite. The results of the analysis are shown in Figure 2.

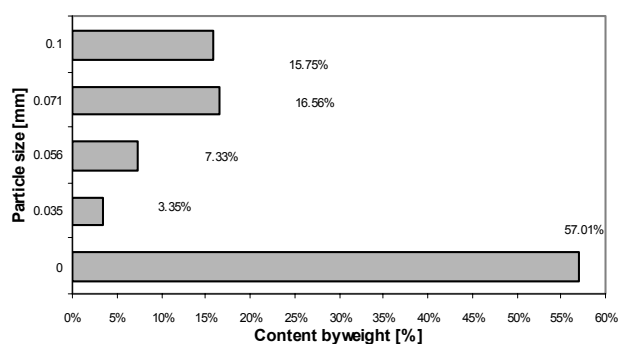


Fig. 2. Particles size distribution of powder filler [25]

As it results from figure the biggest part in filler has grains with size smaller than 0.035 mm. After the stage of preliminary tests fundamental research were carried out. In particular it was the static tensile test, impact measurement, determination of abrasion resistance and friction coefficient.

3.1. Static tensile test

Strength tests were performed according to standard PN-EN ISO 527-1. The study was performed with a universal testing machine Instron Measurements were carried out under the following conditions [25]:

- tensile rate 50 mm/min,
- 4 kN force range,
- temperature of 23 ± 1°C,
- dumb-bells type 1A samples,
- five test pieces for each of the prepared compositions.

With the performed measurements maximum tensile strength and elongation at break were specified.

3.2. Impact strength

Toughness measurement was performed using Charpy method. The hammer used for this purpose had the ability to change the nominal impact energy in the range of values 7.5, 15,

25, 50 J. Impact test was performed according to standard PN-EN ISO 179-1:2000. The device with which a test was carried allow for direct reading of energy that was used to fracture the sample. The measurement was carried out according to the following guidelines [25]:

- nominal pendulum energy of 7.5 J,
- angle of falling pendulum 160°,
- temperature of $23 \pm 1^\circ\text{C}$,
- type 1-shaped specimen with a notch A.

3.3. Abrasion resistance

Abrasion resistance test was conducted to determine the influence of the filler and its modifications on abrasion of the obtained composites. The measurement was carried out according to PN-ISO 4649:2007. The test was carried out with the Schopper-Schlobach device. The result of the study was the determination of sample weight loss. The measurement was carried out under the following conditions [25]:

- temperature of $23 \pm 1^\circ\text{C}$,
- abrasive cloth No. 60,
- contact pressure of the sample to the surface of the cylinder – 10 N,
- distance travelled by the sample – 40 m.

3.4. Coefficient of friction

Determination of coefficient of friction has been done on the unit WTP / 1 based on the provided instructions. The device and the guidelines were developed in the Central Mining Institute of Materials Science and Engineering Department. The measurement was carried out under the following conditions [25]:

- temperature of $23 \pm 1^\circ\text{C}$,
- substrate material S13 steel plate,
- sample contact force 20 N to the ground.

4. Results analysis

Presented research results summarizes the previous work carried out in Division of Metallic and Polymeric Materials Processing. In Figures 3 and 4 results of carried strength test are presented. Presented results describe in detail influence of addition of powdered hard coal filler and its modifications on tensile strength and elongation at break. In the graphs used the following markings PA+Z is a polyamide/unmodified hard coal composite, whilst other markings are suitable for polyamide with hard coal modified by suitable coupling agent.

Results analysis show that the main effect on decrease in discussed properties had the content of the filler. As can be observed, there is a significant decrease in these two properties values in relation to unfilled polymer. In general, the organosilicon coupling agents yielded the worst results. However, for applied titanates the best effects were obtained for the contents of 14 and 21%.

The next stage of the analysis was to determine the impact strength, what is shown in Fig. 5.

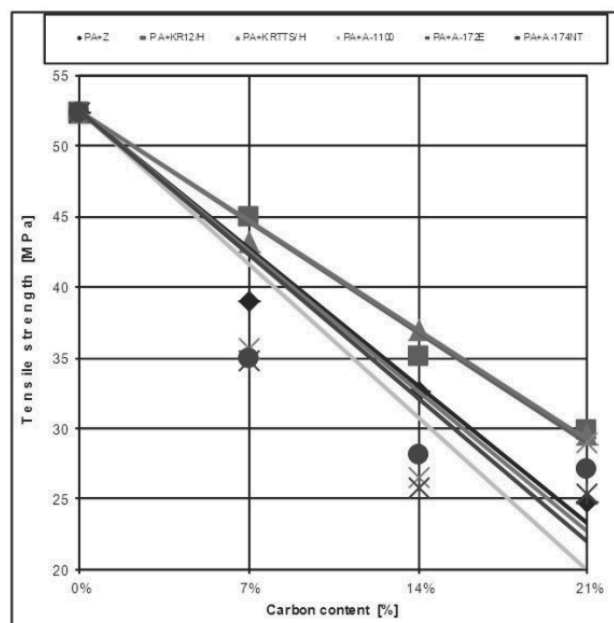


Fig. 3. Effect of filler content and type of coupling agent on the tensile strength

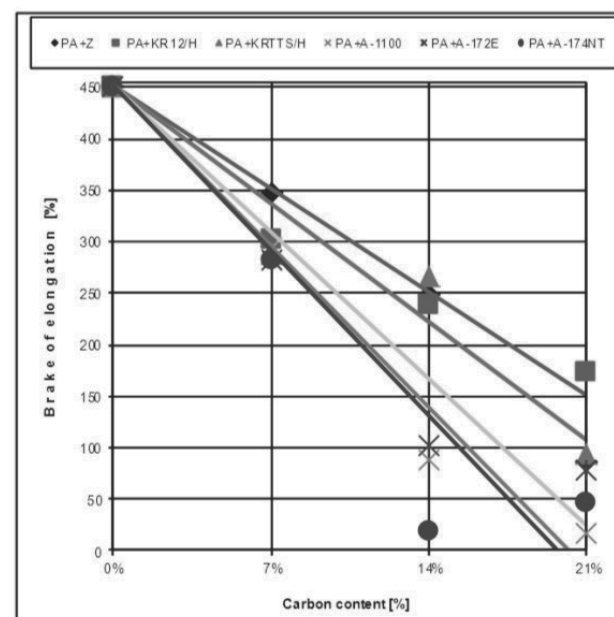


Fig. 4. Effect of filler content and type of coupling agent on the elongation at break

As it results from data analysis increase of filler content results in decrease of toughness values. It can be concluded that the use of organosilicon coupling agents did not result in the formation of binding layer between filler and polymer. At the same time, for titanates better results in properties were obtained, whilst they also show downward trend resulting from filler content.

The results of tribological tests, in particular, wear resistance and coefficient friction are presented in Figures 6, 7.

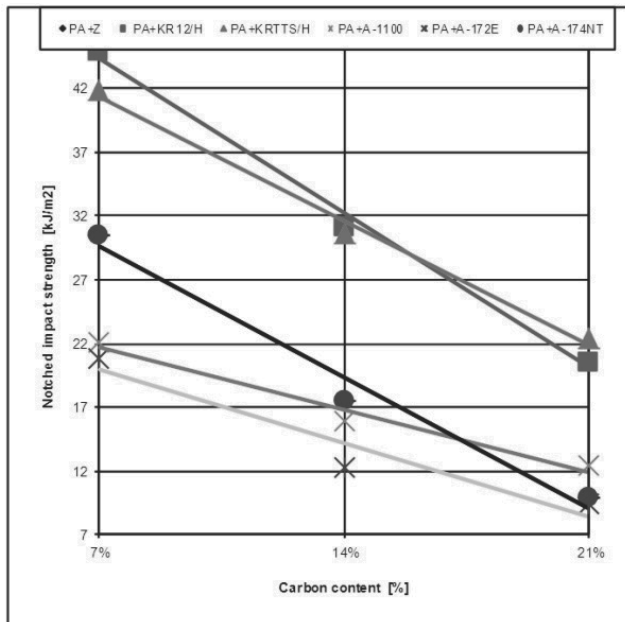


Fig. 5. Effect of filler content and the type of coupling agent on impact strength

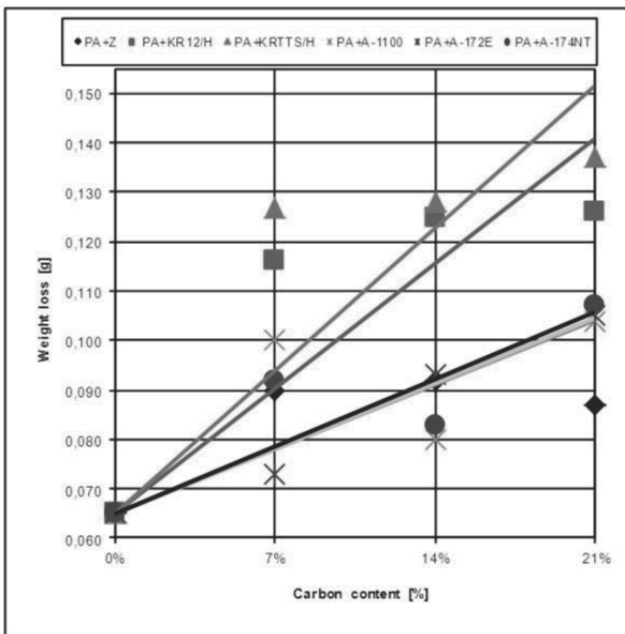


Fig. 6. Effect of filler content and the type of coupling agent on the average weight loss of samples after the abrasion

The analysis of tribological properties leads to the conclusion that composites with filler modified with titanate coupling agents

exhibit the lowest abrasion resistance. On the other side the lowest weight loss factor and in this way the highest abrasion resistance has a composite with filler modified with silane A-172E. At the same time the coefficient of friction showed the opposite tendency: the highest value was observed for the unmodified filler, then the composite with filler modified with organosilicon agents and the smallest for composite with filler modified with titanate adhesion promoters.

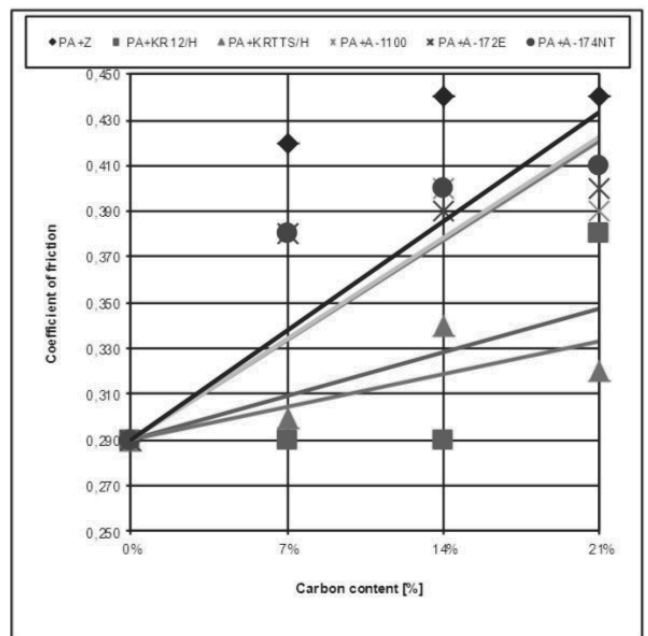


Fig. 7. Effect of filler content and type of coupling agent on the average value of the coefficient of friction

5. Conclusions

The results showed a decrease in both mechanical and tribological properties of polymer/ hard coal composite. The same tendency was observed for both kinds of filler, unmodified and modified with coupling agents. As can be concluded the strongest influence on all properties exhibited filler content. This proves that no positive interaction between filler and polymer was achieved with applied adhesion promoters. Usage of filler surface modifiers did not lead to formation of adhesion bonds and hindered the contact at the polymer-filler interface. It can be concluded that expected adhesive bonds between polymer and filler were not developed. Therefore, there is necessity undertake further research with another coupling agents as modifiers of hard coal filler surface. The task is very difficult because chemical nature of hard coal is very complex. Coal chemistry depends not only on its type but also on the place where it is mined. Because typical coupling agents demonstrated no effect or even deteriorated searched properties in future research it is planned to investigate in detail chemical nature of applied hard coal and then to match surface modifiers to this nature.

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