

Mechanical properties of polyamide matrix composites filled with titanates modified-coal

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Materials

ABSTRACT

Purpose: This article presents the influence of the type of coal surface modifier on mechanical properties of polyamide 6 filled with hard pulverized coal.

Design/methodology/approach: Before preparing compositions, pulverised filler surface was modified with coupling agents. The composite of polyamide 6 and modified hard coal was compounded using a twin-screw extruder. A blend was granulated and later test samples were performed on injection moulding machine. 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 didn't have 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 is planned to be applied 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

World energy deficit, economic balance and environmental considerations leads plastics manufacturers for deeper analysis of fillers have been used. This analysis is limited not only to

compare prices and filler material, but also takes into account the cost of energy consumption and faster machines during processing of composites. For this reason, throughout the world are carried out numerous studies on the impact of: the type and amount of filler, the form of filler, the size of powder fillers particles, impact the surface of the filler and its surface

modification on the properties of composite materials obtained in relation to the cost of production of the composite. An important factor is to determine the feasibility and cost of disposal of used materials.

The purpose of this study is to determine the applicability of natural organic material which is fossil carbon as a filler for thermoplastic polymers and to highlight areas of competitiveness in relation to the materials currently used.

Modification of the polymer is intended to improve the mechanical characteristics, giving new properties – such as discoloration, reducing flammability of the polymer, increase the electrical conductivity – or a reduction in the price of the final product. In addition, introduced into the polymer modifiers, in particular fillers, significantly affect the technological – processing properties the resulting material.

The use of fillers requires knowledge of their basic characteristics, especially the chemical composition, grain composition, shape, surface development, the correlation between the macroscopic and microscopic properties and knowledge of polymer-filler interaction and its impact on the morphology and molecular dynamics of polymer chains in the mixtures of polymer / filler as well as the impact on the properties of the filled polymers. This knowledge is a source of information about the processes running at the interface of polymer/filler and in the polymer phase, surrounding the filler particles as well as the influence of filler on the kinetics of cross-linking of the cross-linked polymers.

Fillers are divided in terms of [1]:

- The origin and chemical structure – into the organic and inorganic,
- The way it affects the polymer – into the active, semi-active and inactive,
- The geometric form – into the lamellar, spherical, irregular and fibrous.

In assessing of the activity of the fillers it is necessary also to take into account the type of polymer, in which the filler is dispersed and the interaction between the polymer and the filler surface. This interaction is particularly important when the mechanical properties of filled polymers are assessing. In addition, important roles by the filler form and its quantity, particle size and dispersion, surface area and fractal dimensions are played [2]. Due to the effects of interaction of the filler with the polymer, for each polymer the filler type is chosen very carefully as well as its quantity and granulation.

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 fraction at least 10%. Presently, in commercial use there are fillers of polymer matrixes in a form of different fibres and powders.

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 [3-6].

There are inorganic and organic fillers [1, 2, 9]. Inorganic fillers are materials in solid form, the composition of which is dominated by inorganic compounds. These fillers may be amorphous or crystalline structure. In the past obtained exclusively from natural raw materials, now being produced by

chemical synthesis. The most commonly used inorganic fillers are silica, alumina, mica, kaolin, glass beads, chalk.

Inorganic fillers are cheap, but are characterized by relatively high mass density – an average of about 2.5 g/cm³ (quartz powder 2.6 g/cm³), in addition, inorganic fillers are hard and can lead to plasticizing systems (cylinder, screw), pressure extruder heads and mould premature wearing [1].

Organic fillers – are mostly natural materials. The most widely used organic fillers are wood flour, starch, fibre, cotton, flax and sisal, jute and cellulose. These measures usually introduced into the moulding compositions based on thermosetting resins, it is only in recent years, the attempts are being made of using of these fillers in conjunction with the thermoplastic materials. The disadvantage of these fillers is limited heat resistance, while the main advantages are low price, availability, low density and ease of recycling [1, 2].

There has been recently an increasingly popularity of fillers derived from synthetic fibres with a chemical structure based on macromolecular compounds observed. These include polyester fibres, polyamide, aramid and carbon fibres.

Coal is a fossil organic material. Compared to many raw materials and natural polymers it is characterized by much higher heat resistance. Decomposition of organic matter of brown coal takes place in the 200-350 °C, bituminous coals in the range 300-500 °C and the anthracite coals 400-600 °C. This may prove advantageous feature in terms of the use of coal as a filler for polymeric materials.

The introduction of carbon into the polymer in the form of filler particles requires a basic knowledge of its properties and structure, predicting the possible interaction with the polymer. In [7] are a few reports on the use of fossil coals for the filling of thermoplastics. These studies have aroused great interest, but for the specific type of coal – from Russia (Karelia). The content of chemical element C in this type of coal is to 98%, and it is rich in carbon fullerenes.

In the research of the fossil carbon uses as a filler for thermoplastics alkylated coal has been used. Known is the widespread use of other carbon materials as fillers such as graphite, diamond, carbon black, coke, but they are usually expensive and obtained by chemical processes rather than simple processing of natural raw materials.

The use of fillers is conditional on the provision of adequate co-operation at the interface of the filler - matrix. Phenomenon on the border of the two phases is adsorption. It consists in the fact that the phase constituents present in different quantitative molecular relations in the boundary layer than in the depths of the material. This phenomenon is caused by asymmetric distribution of forces at the interface [12].

The amount of the component has been adsorbed depends on the properties of adsorbent, surface developing and its properties, kind of adsorbent, its concentration and the temperature and pressure. Depending on the type of forces between the adsorbent and the adsorbed substance (adsorbate) physical and chemical adsorptions are distinguished [12].

Physical adsorption is caused by Van der Waals forces and is reversible, and during the process releases a small amount of heat.

Chemical adsorption, also called chemisorption occurs as a result of the formation of chemical bonds. It is usually an irreversible process or in part reversible. In this case, the heat

absorption of the chemical reaches a value comparable with the chemical reaction warmth.

Properties of polymers in the boundary layer are different from those at the depth of the material due to differences in the molecular weight distribution, degree of crystallization and morphology of the overmolecular structures. For compositions comprising two or more polymers, the part of them is in the interlayer between the phases, so it is important to know the exact structure of this layer. During the first mixing of the composition of plastic the adsorption binding of macromolecules from the surface of the filler occurs.

This process is important and affects the adhesion of polymer to the filler. As a result, the surface layer is formed. The ability of the polymer to surface adsorption of the filler determines not only the properties of the boundary layer, but also the nature of adhesive interactions and thus the strength of the composite [12].

Typically, the components with the highest surface activity are adsorbed, so changes the probability of occurrence of the individual components of the composition at various points around the filler. This affects a large extent on the course of chemical reactions with the filler and between components of the composition, and is the cause of heterogeneity in the structure and properties of the surface layer.

The second phenomenon is the interfacial adhesion strength defined as a force occurring between the surfaces of different bodies [12]. This is due to intermolecular interactions (dispersive and dipole), ion-dipole interaction, hydrogen bonding or strength of chemical bonds. Low adhesion occurs when the materials characterized by an uneven surface, because the materials are adjacent only at certain points. To increase adhesion of material's parts is required to bring at least one external layer of them to plastic or high plastic state and pressed them together.

High bond strength of polymer phase with each other and with the filler included in the composition is the indispensable condition for obtaining good properties of products will be made with.

From the standpoint of physical chemistry and induce adhesion forces occurring at the boundary phase, which affect the adsorption of macromolecules. Therefore, adhesion of the polymer depends on the conditions of its adsorption on the surface of the filler. This follows from the fact that the flexibility of macromolecular chains and changes in their conformation in the adsorbed polymer layer on the adhesion effect.

Adhesive bond strength depends on the interfacial layer deformability, because to a large extent it depends on the concentration of the stress of the material during use. Increased binding energy of a polymer with a filler and a greater number of contact, increases the rigidity of macromolecules.

It is therefore appropriate modification of fillers introduced into the polymer matrix is so important for enhances the hydrophilicity of the filler. For the purpose of this work, as a coupling agent was used titanates. Extras coupling molecular compounds are causing a better combination of two ingredients, usually though it is not the rule, one of compounds is an inorganic filler and the second one is called resource base – its main component is a polymer.

The addition of a coupling agent which are titanates, to the compositions based on polymers, causes the most improved adhesion, strengthening of the catalytic reaction, improves the dispersion, impact resistance and mechanical properties. Thanks

titanates in many cases filling ratio of inorganic compounds can be increased up to 50%. The reactions are possible using different ingredients such as calcium carbonate, barium sulfate, carbon black technical, nitrates, hydroxides, phthalates, carbon fibres, etc. In general, it can be organic ingredients and polymers, pigments, and the typical minerals and metal oxides [15].

Titanates are offered in three forms [17-20]:

- Liquid – Ken-React LIC (liquid coupling ingredient),
- Powder – Ken-React Kapos (powder coupling ingredient),
- Granular – Ken-React CAPS (granular coupling ingredient).

They offer many advantages including elimination of the additional processing to prepare the filler, are used in small quantities, generally from 0.2 to 1% by weight, are added directly to the compound [15]. In addition they make possible to improve property such as:

- resistance to UV and X radiation,
- bending strength,
- resistance to tensile stress,
- durability of parts,
- corrosion resistance,
- viscosity reduction,
- increase the checks in the process of catalysis, thus giving the better flow for a reinforced polymers.

They are used as a coupling agent for fillers found in most plastics processing, such as glass fibres, carbon fibres, PTFE and other organic [20].

In the present study is possible to observe attempts to examine the possibility of unenergetic use of coal as a natural organic material located in large quantities in Poland and abroad. Aim of this study is to determine the property of a nylon-filled composite material, fossil carbon modified, as well as the influence of respectively modified carbon on the density, tensile strength, impact resistance.

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 powder filler of polyamide 6 is shown in Table 1.

Table 2.
Hard coal physical properties

Density [g/cm ³]	Coal type 35				
	Chemical composition [wt%]				
	C	H	O	N	S
1.33	88.46	4.68	4.46	1.87	0.52

To modify the hard coal surface are used [28]:

- **Ken-React CAPOW KR 12/H** – (titanate) Includes: 65% KR 12 / H ((Tris (dioctylphosphato-O⁻) (propan-2-olato) titan) and 35% silicon dioxide,
- **Ken-React CAPOW KR TT S/H** (titanate) – Contains: 65% KR TT S / H ((Titan-IV 2-propanolato, tris (isooctadecanoato-O⁻)) and 35% silicon dioxide.

In Tables 2 and 3 physicochemical properties of the above-mentioned coupling agents are presented.

Table 2.

Physicochemical properties of titanate KEN-REACT KR 12/H [18]

Appearance	Form	solid, powder
	Color	bright yellow
Odor	characteristic	
safety data	Melting temperature	indefinite
	Boiling point / range	71 [°C]
	Ignition temperature	148 [°C]
	Vapor pressure	does not affect
	Density	indefinite
	Solubility	insoluble in water
	pH	4-6
	Dynamic viscosity	>1000 cps

Table 3.

Physicochemical properties of titanate KEN-REACT KR TTS/H [17]

Appearance	Form	solid, powder
	Color	white
Odor	fatty	
safety data	Melting temperature	indefinite
	Boiling point / range	148 [°C]
	Ignition temperature	93 [°C]
	Vapor pressure	Doesn't affect
	Density	0.95 [g/cm ³] (20 °C)
	Solubility	10 [g/l]
	pH	7
	Dynamic viscosity	125 cps

2.2. Preparation of samples

Test samples were prepared in two steps. In the first stage extruder pellets were prepared for the assumed carbon content of fossil, modified with titanates. The second stage involved an injection of samples subjected to static tensile and impact test.

The composition containing 7%, 14% and 21% of fossil carbon has been taken. Due to the preparation of the composition of a fossil carbon content not exceeding 40% of the total weight

of the mixture, which is required to use from 0.4% to 1% by weight of coal, for modifications to 1% of Ken-React KR 12 / H or 1% of Ken-React KR TT S / H parts by weight was received. Titanates was introduced by manual mixing in a container to draw saponification-charges. In the case of filling in excess of 40%, according to the literature, is proposed to increase the dosage of the modifier up to 2.5% by weight of filler.

The process of preparing of the composition was performed using a two screw extruder, the "Leistritz" company, in the Central Mining Institute in Katowice.

Preparation of the material consisted of drawing up a control mass with a total weight 200 g, in which they are entered PA6 pellets and pulverized coal with a content of 7%, 14%, 21% parts by weight, pre-mixed with the Ken-React KR 12 / H, or Ken-React KR TT S / H.

The control mass quantity has been prepared on the scale of accuracy of 0.1 g. Prior to extrusion was also measured bulk density. In addition, for comparative purposes pure polyamide 6 with 1% of Ken-React KR 12 / H or 1% of Ken-React KR TT S / H parts by weight was presented.

The following Table 4 lists the parameters of the extrusion composition.

Table 4.

Parameters of extruder

Extrusion parameters	Composition	
	PA+KRTTS/H	PA+KR12/H
Torque [% max. torque]	25	73
Mass pressure [bar]	21	20
Mass temperature [°C]	226	220
Screw rotation [rpm]	200	200
Yield [kg/h]	8	10
	PA+7%Z+KR1 2/H	PA+7%Z+KRT TS/H
Torque [% max. torque]	73	74
Mass pressure 1 [bar]	32	28
Mass temperature [°C]	220	222
Screw rotation [rpm]	200	200
Yield [kg/h]	10	10
	PA+14%Z+KR TTS/H	PA+14%Z+KR 12/H
Torque [% max. torque]	75	77
Mass pressure 1 [bar]	27	29
Mass temperature [°C]	222	187
Screw rotation [rpm]	200	200
Yield [kg/h]	10	10
	PA+21%Z+KR 12/H	PA+21%Z+KR TTS/H
Torque [% max. torque]	73	79
Mass pressure 1 [bar]	30	34
Mass temperature [°C]	219	221
Screw rotation [rpm]	200	200
Yield [kg/h]	10	10

Temperatures in different zones of the cylinder from filling up to the nozzle was fixed for each control mass portion, any even minor changes were immediately corrected by the computer operating extruder.

In order to obtain granules the rod formed in the extrusion process have been granulated on a laboratory granulator knife.

Prior to the injection process, plastic granules have been obtained was subjected to 48 hours drying process in a laboratory drier at 80 °C.

After the pellets drying, the samples in the shape of dumbbell, using injection moulding processing were made with help of the injection moulding machine ARBURG, located in the Central Mining Institute in Katowice. Process parameters are summarized in Table 5.

Table 5. Parameters of injection moulding

Process parameters	Polyamide 6	Filled Polyamide 6
Mold temperature [°C]	60	60
Injection rate [cm ³ /s]	25	25
Pressure in the form [bar]	650	500-600
The pressure switching time [s]	0.3	0.3
Holding pressure [bar]	350	350
Holding pressure time [s]	15	15
Cooling time [s]	9	9
Dosing [cm ³]	32	32
Temperature in zones, from the embankment [°C]	250-260-300	255-265-305

The samples, prepared in the form of paddles, before testing have undergone of the accelerated process of conditioning in water at 70 °C for 8 hours. Conditioning was conducted in a laboratory drier in the Laboratory of the plastics processing industry of Metal and Polymer Materials Processing Plant. Samples in the form of paddles after conditioning were used to perform static tensile tests, as well as to prepare profiles for the impact test.

For the impact test, in accordance with BS EN ISO 179-1 norm, profiles of length of 80 ± 2 mm, width of 10 ± 0.2 mm and thickness of 4 ± 0.2 mm, with a milled notch in the middle was prepared.

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 INSTRON 4465 , it located

in Central Mining Institute in Katowicach. 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.

Density

The study was conducted in the Laboratory of the Department of Materials Science Central Mining Institute, in accordance with standard PN-92/C-89035. The aim was to determine the density measurement of samples made of nylon with coal filled and titanates as coupling agents. Measurement has been effectuated by weighing of the sample, using an analytical balance Mettler Toledo, which automatically calculate the density of samples by performing firmware. As the immersion liquid distilled water at 24.5 °C, and density of 0.997 g/cm³ was used.

3. Results and discussion

The results of the sieve analysis of particle size distribution are presented in Table 6 [21].

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.

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 three basic strength and deformation characteristics: tensile strength, elongation at break, and elongation. The first three characteristics were presented in graphic form in Figures 1, 2 and 3.

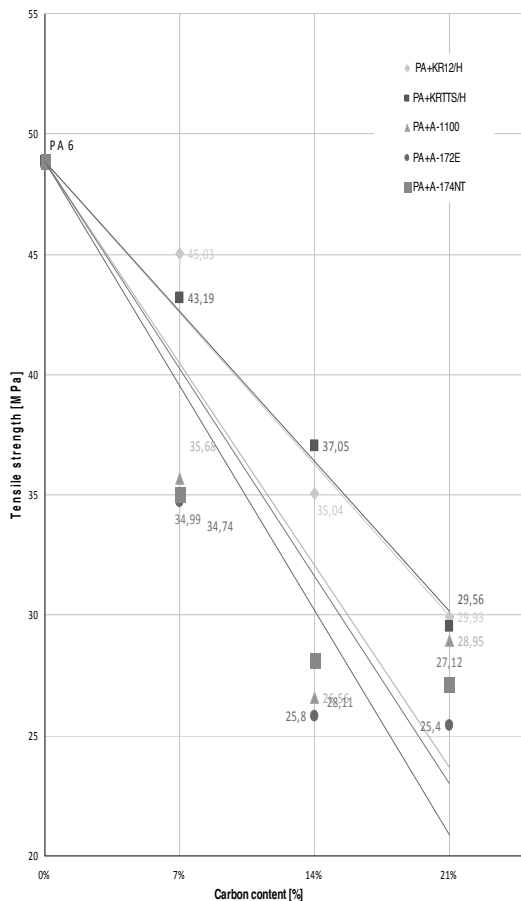


Fig. 1. Effect on content of a filler and a type of titanate and silane on the tensile strength

Presented results are the average of five measurements. The results were related to the work [22], in which hard coal with the help of silanes was modified.

As is clear from the analysis results indicated in Figure 1, the major impact of a decrease in tensile strength has a content of filler in the composition. There is a linear decrease in strength values for the carbon content between 0% and 21% share in the composition, but only in the case of modifying agent KRTTS / H.

However, for the titanate KR12 / H results seem to be less predictable with increasing filler content, because the strength is changed by 10 MPa or 4 MPa. Despite this noticeable is the occurrence of a similar inclination of the trend line in both these cases. Comparing the means of modifying fillers can be seen that tensile strength of silanes is deteriorated in comparison with titanates by 30% at 14% filler content.

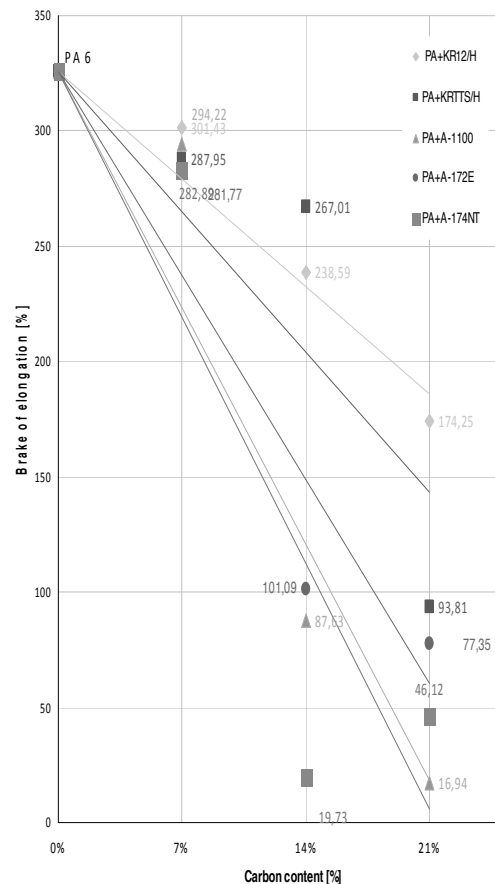


Fig. 2. Influence of carbon content and a type of titanate and silane on elongation on break

Influence of coal and the type of modifying agent on elongation and elongation at break were presented sequentially in Figures 2 and 3. Both the decrease in elongation at break, and the relative elongation in tensile strength are principled and highly influenced by filler content.

You will notice a significant difference between the set of titanates, and silanes. The compositions with the modifying agents KRTTS/H, KR12/H, A-1100 and A-174NT for relative elongation at tensile strength behave similar trend lines, which you cannot write about silane A-172E. Interesting results were observed in 21% of titanates modified-coal filler, where the elongation at tensile strength drastically decreased to a value of 8.71% for KRTTS/H, which gives a result worse than during the tests performed on silanes. Similar declines are observed for the filler content of 14%.

3.2. Impact strength results

The result of measurement is an average value of the adjusted impact energy. In addition, the chart (Figure 4) were placed on the results from the analysis of the composition with other coupling agents - silanes [22].

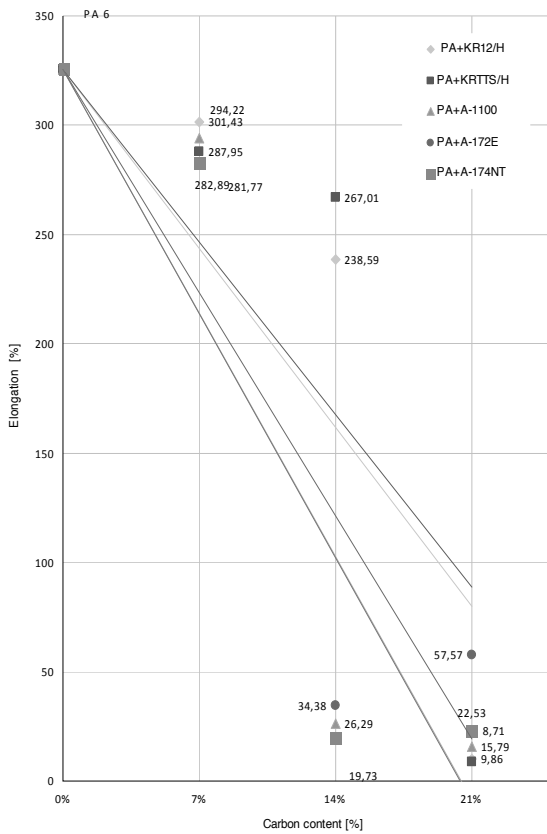


Fig. 3. Influence of carbon content and a type of titanate and silane on elongation

As can be seen from Figure 4 shown a decrease of toughness is closely related to the increase in the percentage of carbon content in the composite. As can be inferred from the results obtained, the nature of the surface modifier has an effect on the values toughness.

The essential differences are noticeable for the content of 7% and 21% filler content. At the same time comparing the results of toughness silanes are significantly lower compared to the titanates.

The composite containing 21% carbon tytanianami modified to have a similar impact strength value at a composition with the applied silanes of 7% carbon content. The slope of the trend line for the titanate is larger, and therefore can be predicted that further increasing the carbon content drastically decrease the toughness of the composite.

The use of coupling agents in the form of titanates increased the impact strength compared to compositions in which the surface modifier were all kinds of silane used for all filler percentages.

At the same time it should be noted that the reduction of the impact may be closely associated with the formation of agglomerates of filler in the polymer matrix, which act as internal notches, effectively worsening the impact properties of the composite.

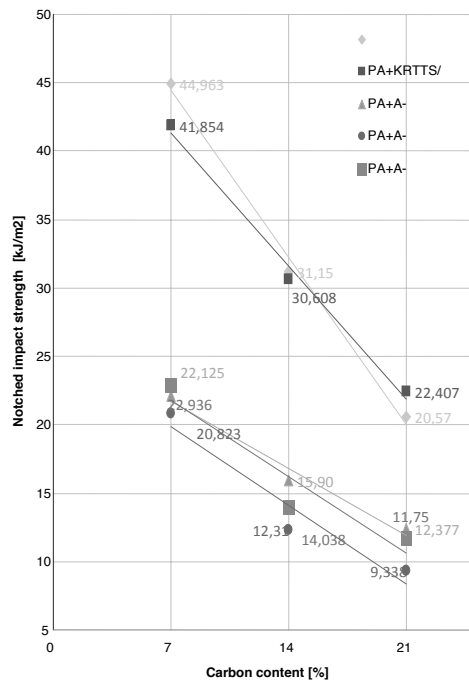


Fig. 4. Influence of carbon content and a type of titanate and silane on notched impact strength

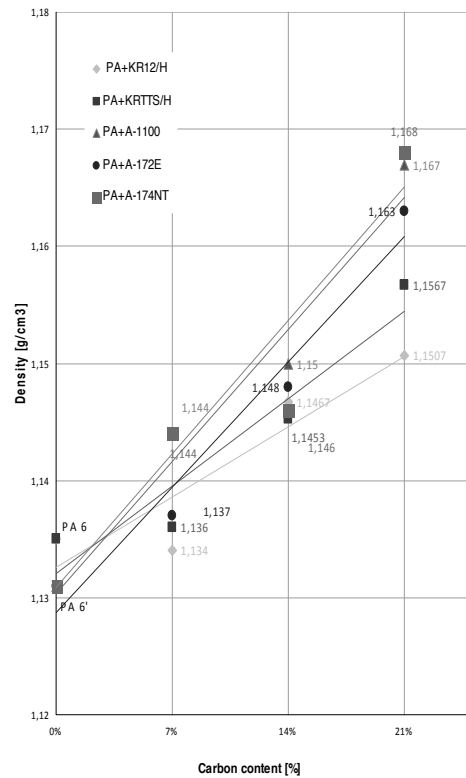


Fig. 5. Influence of carbon content and a type of titanate and silane on density

3.3. Density results

Density measurements are shown in the chart – Figure 5. Influence of the kind of titanate or silane and pit-coal content on the density of the composite filled illustrated here. In each case, a noticeable increase in a composition density is linear in relation to the increase of the percentage of filler. It is worth noting that the composite density in the case of titanates and 7% containing of the filler has a similar value as for the pure polyamide, such a state is most likely related to measurement error during the test.

Such small differences between the trend lines for different coupling agents let ones to formulate the conclusion that they do not affect significantly the density of the composition. Differences between the compositions are about 0.01 g/cm^3 .

4. Conclusions

Based on the investigations have been realized can be concluded that:

1. Major impact on the reduction of mechanical properties of polyamide composite material with pit-coal filled, has a degree of filling,
2. Mechanical properties of polyamide, filled with the pit-coal modified with titanates, are higher compared with the case of silanes,
3. Toughness decreases with increasing of filler content, such as mechanical properties, which may result from the lack of an adequate filler homogenization level with the matrix,
4. The type of the coal surface modifier does not affect on the density of the composite.

References

- [1] H. Seatchling, Plastic Guide, WNT, Warsaw, 2002 (in Polish).
- [2] K. Kelar, Physical chemistry of polymers, University of Technology Publishing House, Poznan, 1997 (in Polish).
- [3] J. Nabiałek, J. Koszkuł, The polymers flow in a mould cavity during the injection moulding process. Comparison of an experiment and computer simulations, Proceedings of the 12th Scientific International Conference „Achievements in Mechanical and Materials Engineering” AMME’2003, Gliwice – Zakopane, 2003, 641-644.
- [4] Ł. Suchoń, J. Stabik, M. Rojek, M. Szczepanik, Investigation of processing properties of polyamide filled with hard coal, Journal of Achievements in Materials and Manufacturing Engineering 33/2 (2009) 142-149.
- [5] J. Stabik, A. Dybowska, Electrical and tribological properties of gradient epoxy-graphite composites, Journal of Achievements in Materials and Manufacturing Engineering 27/1 (2007) 39-42.
- [6] D. Ozimina, Plastics and composite materials, Kielce University of Technology Publishing House, Kielce, 2006 (in Polish).
- [7] P. Wasileski, Chemistry and chemical technology of coal, Silesian University of Technology Publishing House, Gliwice, 1984.
- [8] M. Szczepanik, J. Stabik, Review of polymer composite materials with coal filler, Silesian University of Technology Publishing House, Gliwice, 2008 (in Polish).
- [9] A. Boczkowska, J. Kapuściński, Z. Lindermann, Composites, OWPW, Warsaw, 2003 (in Polish).
- [10] L.A. Pilato, M.J. Michno, Advanced composite materials, Springer-Verlag, Berlin, 1994.
- [11] J. Stabik, Selected issues of filled thermoplastic rheology, Silesian University of Technology Publishing House, Gliwice, 2004 (in Polish).
- [12] B. Jurkowski, B. Jurkowska, Preparation of polymer compositions. Elements of the Theory and Practice, WNT, Warsaw, 1995 (in Polish).
- [13] A. Eichert, Z. Kornetka, Role of coupling agents in system polymer filler, Polymers – High molecular mass materials 5 (1997) 331-336 (in Polish).
- [14] T. Broniewski, Methods of researching and appraising polymer materials properties, WNT, Warsaw, 2000 (in Polish).
- [15] Solvadis Poland, Plastics Review, Advertising materials, May 2006.
- [16] J. Stabik, A. Dybowska, Methods of preparing polymeric gradient composites, Journal of Achievements in Materials and Manufacturing Engineering 25/1 (2007) 67-70.
- [17] A. Gnatowski, J. Koszkuł, Investigations of the influence of filler on the properties of chosen polymer blends with compatibilizer addition, Proceedings of the 13th Scientific International Conference „Achievements in Mechanical and Materials Engineering” AMME’2005, Gliwice – Wisła, 2005, 247-250.
- [18] Characteristic card Ken-React KRTTS/H, 2009.
- [19] Characteristic card Ken-React KR12/H, 2009.
- [20] Ken-React Reference Manual, Titanate, Zirconate and Aluminate Coupling Agents.
- [21] Ł. Suchoń, Mechanical properties of polyamide filled with hard coal, Chemist, 2008.
- [22] T. Cieślak, The mechanical properties of polyamide filled with modified hard coal, Master’s thesis, Gliwice, 2009.