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Mechanical and electrical properties of mined coal filled polyethylene and polyamide

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ABSTRACT

Purpose: The purpose of the present paper is to present results of basic mechanical properties research of high-density polyethylene and polyamide 6 filled with two kinds of mined coal particles. Because composites with carbon are expected to poses low electric resistance also surface resistivity was measured.

Design/methodology/approach: Dependences of tensile strength, elongation at break, impact strength, ball hardness and surface resistivity on volume content of mined coal in polymeric matrix are measured and discussed.

Findings: Introduction of mined coal fine particles to polyethylene did not cause significant changes in tensile strength, while the same property of polyamide composites decreased significantly. Brinell ball hardness of all polyethylene and polyamide composites increased almost proportionally to coal content. Pronounced lowering of deformability (elongation at break) with increasing coal content was observed for all formulations. Also impact strength significantly decreased after mined coal filling. Significant lowering of surface resistivity was noticed especially for coal-polyamide composites.

Research limitations/implications: Obtained results showed that mined coal fine particles can be applied as a filler of thermoplastic polymers but poor adhesion between polymer matrix and filler particles was achieved. Additional research on mined coal fine particles modification by coupling agents is needed to develop better adhesion.

Practical implications: Obtained results showed that mined coal fine particles can be applied as a filler of thermoplastic polymers but poor adhesion between polymer matrix and filler particles was achieved. Additional research on mined coal fine particles modification by coupling agents is needed to develop better adhesion.

Originality/value: Polymer composites with carbon as a modifier has been used for many years but there have been only a few experiments on introducing fine particles of mined coal into thermoplastics.

Keywords: Mined coal; Filled polymers; Polymer composites; Mechanical properties; Surface resistivity

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PROPERTIES

1. Introduction

Filled polymers are more and more widely applied as engineering composites. Hard particles and carbon between them have been used in polymer composite materials for many years [1-11]. The forms of carbon introduced most frequently into polymer matrixes are short and long carbon and graphite fibres, carbon black and graphite particles. Sometimes coke and diamond powders are also applied but only in research programs not in

industrial applications. There have been very few experiments on introducing mined hard and brown coal into thermoplastic polymers [7,12].

Mined coal belongs to one of organic raw materials widespread in Poland and in the world. In comparison to many other raw materials it is cheaper and easier to achieve [7,13,14]. As a potential polymer filler very attractive is also its high thermal resistance and low electrical resistance. Thermal decomposition of brown coal organic matrix take place in the temperature range from 200°C to 350°C, bituminous coal decomposes from 300°C to 500°C and anthracite coal from 400°C to 600°C. Chemical composition and structure of mined coal is very complex, much more complex then of other organic fillers.

Reasonable introduction of mined coal into a polymer matrixes requires basic knowledge of its characteristics and structure [7,15]. Mined coal is not an allotropic form of carbon element. Chemically it is very complex and heterogeneous material, including organic and inorganic part. Heterogeneous structure of mined coal is a result of geological and thermodynamic conditions during its formation process history. For the structure of mined coal very important is also organic precursor from which it was formed. The structure and composition differ form type to type and depends on the place of its mining. Many research programs were dedicated to understanding chemistry of coal and different models of its structure were proposed. Now, taking into account results of elementary chemical analysis, analysis of functional groups, analysis of extraction, pyrolysis and oxidation products, coal researchers indicate that it has three-dimensional structure and that structure of coal mined in various places in the world differs very substantially [15].

Very few research results concerning mined coal fine particles used for filling thermoplastics have been published up till now in the literature. That research applies mainly to a specific kind of coal from region Karelia in Russia. The percentage content of the C element in this coal is up to 98% and very high is fullerene particles content [16-18]. There were also attempts to apply allylated coal as a polymers filler [18]. Very interesting results were obtained when introducing mined coal fine particles into epoxy resins [19,20]. Presently a research programme is realizing concerning introduction of mined coal fine particles into thermoplastic polymers [7,21].

In the present paper results of research on basic mechanical properties of high-density polyethylene and polyamide 6 filled with two kinds of mined coal fine particles are presented. Because carbon in the mined coal form is expected to lower electric resistance of composites also surface resistivity was measured. On the present initial stage of research, filler's surface modification was not considered.

2. Experimental

2.1. Materials used

ATOFINA Finathene 5502 high density polyethylene and Tarnamid T27 polyamide 6 produced by Zakłady Azotowe in Tarnów (Poland) were used as matrixes. Two kinds of coal (marked A and B) were used as fillers: hard coal (A) with 83.6% content of the C element from the "Bielszowice" mine (Poland) and anthracite coal (B) with 93.5% content of the C element from the "Wiktoria" mine (Poland). Both coals were ground and sieved through a 0.1 mm screen. The fillers were introduced with respectively 7, 14 and 20% of volume.

Results of chemical constitution [16] and density tests of applied coals are presented in the Table 1. In the Table 2 results of particle diameter and particle aspect ratio distributions are given.

Table 1.
Chemical constitution and density of hard (A) and anthracite (B) coal

Coal type	Elementary analysis, $\%^{daf*}$			Technical analysis,	
	C	H	O+N+S	Ash % weight	Density g/cm^3
Hard (A)	83.6	4.51	11.89	3.6	1.38
Anthracite (B)	93.5	2.7	3.8	7.4	1.45

* ^{daf} - element content without moisture and ash

Table 2.
Results of particle diameter and aspect ratio distributions analysis

Coal type	Diameter			Aspect ratio		
	Range μm	Mean value μm	Modal value μm	Range	Mean value	Modal value
Hard (A)	4-34	8.00	10.94	1.0-2.4	1.46	1.45
Anthracite (B)	4-40	10.91	10.62	1.0-2.6	1.52	1.51

2.2. Composites preparation

Composites were prepared by extrusion method using single screw extruder with mixing zone at the end of screw. Polyethylene composites were extruded at 190°C and polyamide composites at 230°C. To avoid differences in deformational history, polymers without fillers were processed in the same manner and in the same conditions.

2.3. Measuring procedure and results

A static tensile test, an impact test, a hardness test and surface resistivity measurement were conducted. All test samples were injection moulded. PA test pieces were additionally conditioned at water at 90°C during 4 hours after moulding.

The tensile test was conducted according to the EN ISO 527-1 standard, with use of a Haeckert FPZ 100/1 tensile test machine. Measuring conditions are given in the Table 3. Tensile strength (Rm) and ultimate elongation at break (ε) were determined. Six test pieces were used for all composites. The mean results are presented in the Table 4.

Table 3.
Conditions of performed tests

Test	Test conditions	Composites	
		Polyethylene composites	Polyamide composites
Tensile test	Velocity, mm/min	50	10
	Force range, N	0-2 000	0-10 000
	Temperature, °C	23°C±1°C	23°C±1°C
Impact test	Hammer energy, J	1	5
	Hammer velocity, m/s	2.93	2.93
	Temperature, °C	20°C±1°C	20°C±1°C
Brinell hardness test	Ball thrust, N	132	357
	Ball diameter, mm	5	5
	Temperature, °C	21°C±1°C	21°C±1°C
Surface resistivity measurement	Voltage, V	1000	500
	Temperature, °C	21°C±1°C	21°C±1°C

Table 4.
Comparison of achieved tests results

Composite		Properties [1]						
Type of composite	Coal content	Rm	ε	U_N	U	HB	ρ	R_S
	%	MPa	%	kJ/m^2	kJ/m^2	MPa	g/cm^3	10^9 Ω
Polyamide								
PA	0	40.23	106	43.5	-	100	1.1369	3.73
PA + coal A	7	36.96	16.09	16.1	29.9	105	1.1547	2.56
	14	29.38	11.09	13.7	26.6	109	1.170	2.31
	20	22.44	5.57	9.4	16.3	113	1.179	2.13
PA + coal B	7	34.7	15.78	17.3	38.5	104	1.143	3.23
	14	35.52	13.73	11.7	22.5	107	1.157	2.2
	20	34.02	8.86	9.2	22.0	112	1.167	2
Polyethylene								
PE	0	23.77	76	-		48.70	0.939	17.1
PE + coal A	7	23.40	48	9.53		51.37	0.968	14.9
	14	23.21	42	7.26		56.64	0.992	13.2
	20	24.58	24	5.60		61.13	1.017	9.1
PE + coal B	7	23.53	45	8.28		52.14	0.974	16.9
	14	22.46	30	5.54		54.87	0.993	9.3
	20	22.52	15	4.07		60.47	1.016	7.3

1 – Meaning of used symbols is given in the text

The impact test was conducted according to the EN ISO 179-1/1eA standard with use of a Zwick's Charpy impact tester. Impact strength test conditions are given in the Table 3. For polyamide composites test pieces notched (UN) and unnotched (U) tests were conducted. For polyethylene composites only notch impact strength test was possible because unnotched samples did not break. Six tests were performed for all composites. Table 4 presents average impact strength values.

Measuring of ball hardness (HB) was conducted according to the EN ISO 2039-1 standard, with use of a Brinell HPK no. 4/20 plastics hardness tester. Hardness test conditions are given in the Table 3. As for previous tests six measurements were performed for all formulations. Average hardness values (HB) are also presented in the Table 4.

The surface resistivity (R_S) test were conducted according to IEC 60093 standard, with use of high internal resistance meter MER-1. Six measurements were conducted for all materials. Test conditions are given in the Table 3 and average results in the Table 4.

Additionally density (ρ) was measured to check coal contents. It was measured according to PN-92/C-89035 standard, using Mohr method. Results also are given in Table 4.

3. Discussion

Observed influences of mined coal content on mechanical properties depend first of all on type of polymer and in the second place on type of coal. Influence of mined coal particles content and coal type on changes in tensile strength of polyethylene was minimal. Differences between tensile strength of polyethylene composites with growing mined coal content were in the measuring error range. For polyethylene filled with hard mined

coal (A) small strength increase was observed and for polyethylene filled with anthracite insignificant decrease took place. On the other hand for all polyamide – mined coal composites tensile strength values were significantly lower then for unfilled polyamide. For polyamide composite with highest content of anthracite (B) about 15% tensile strength decrease was observed. But for polyamide filled in the same level with hard coal (A) observed strength decrease was about 50% of that value for unfilled polymer. Dependences of tensile strength on the filler content is shown in the Fig. 1. Obtained significant tensile strength decrease indicate that poor bonding between polymer matrix and filler surface was achieved. Especially for polyamide filled with hard coal (A) it is supposed that solid particles introduced into polymer matrix a lot of stress concentration centres and micro-cracks and regions on filler surface with minimal or zero adhesion.

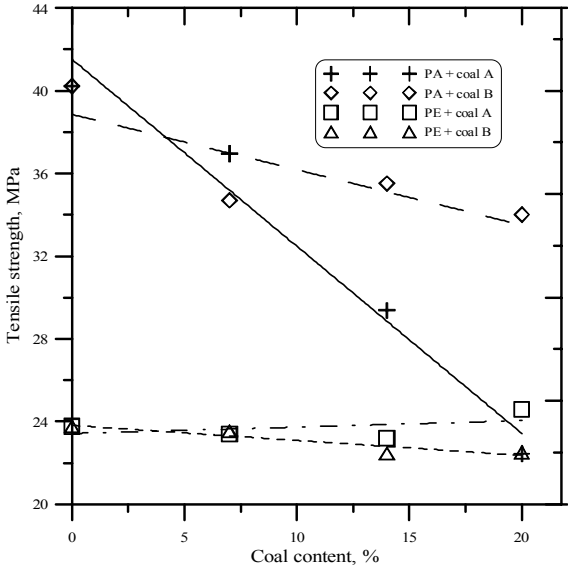

Fig. 1. Influence of mined coal particles content on tensile strength of polyethylene and polyamide composites

Even more significant decrease of deformability expressed by the elongation at break dependent upon increase of the coal content was observed for both polymer matrixes and both types of mined coal particles. Fig. 2 shows all of these dependences. As for tensile strength results, once more polyamide composites exhibited more pronounced decrease. For polyethylene filled with the highest hard coal (A) content elongation at break was about 55% of the same property for pure polymer and for polyethylene filled with 20% vol. with anthracite coal (B) it was only 20%. Even less deformable were polyamide based composites. For polyamide filled with the highest content of hard coal (A) particles elongation at break was about 10% of the same characteristic for unfilled polymer and for polyamide filled with the highest content of anthracite mined coal (B) the analogues percentage was only 8%. The higher was mined coal particles content the more brittle and less deformable became all composites. Composites with the highest mined coal content broke with zero or minimal plastic deformation and sometimes in the fully brittle manner. Elongation at break results once more indicate that poor adhesion between polymer matrix and filler particles surface was achieved. Fillers particles played role of inclusions weakening intermolecular forces important to withstand external forces.

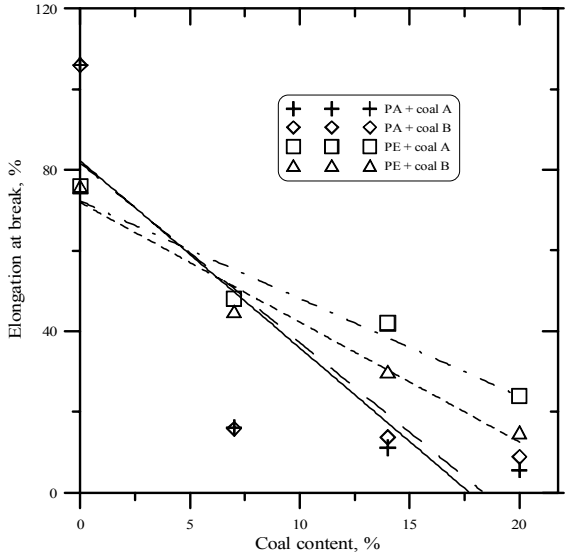

Fig. 2. Dependences of elongation at break on mined coal content for polyethylene and polyamide composites

Tensile strength and elongation at break result indicate that mined coal can not be used as reinforcing agent for thermoplastics such as high density polyethylene and polyamide. Both types of mined coal can be used as cheap extenders for both polymers and ready composites are suitable for those applications where deformability is not very important. Especially interested are results for polyethylene for which only deformability decreased significantly and tensile strength remained almost unchanged. Tensile strength and elongation at break results show also that additional research is needed to achieve better linkage between polymer matrixes and fillers surfaces [1,22]. In the near future experiments are planned on mined coal surface modification by applying surfactants and coupling agents and on properties of composites filled with modified mined coal.

Impact strength, especially notched impact strength, is the second indicator of deformability. Impact strength significantly decreased with simultaneous increase of mined coal content in polyethylene and polyamide. Apart of this many polyethylene composites test pieces, especially with low mined coal content, without notch did not break and results of these tests were not taken into consideration. The same effect was not observed for polyamide composites. Results of impact strength tests for polyamide composites for unnotched samples are presented in Fig. 3. Notched Charpy impact strength results for both polymers and their composites are presented in the Fig. 4.

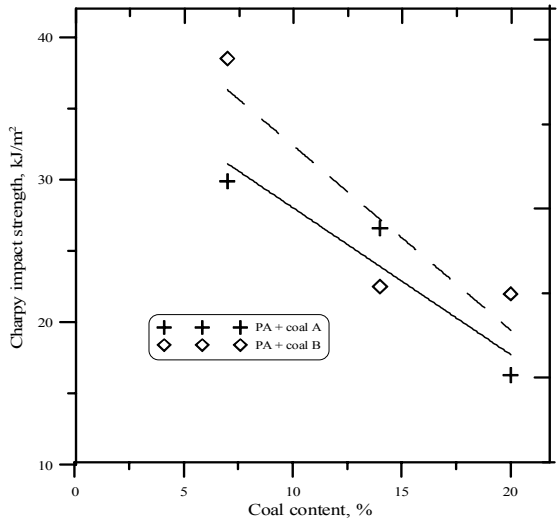

Fig. 3. Influence of mined coal content on impact strength of polyamide composites

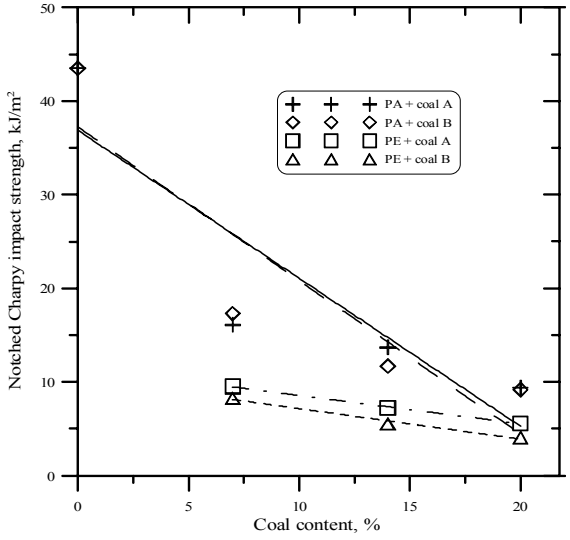

Fig. 4. Influence of mined coal content on notched Charpy impact strength of polyethylene and polyamide composites

All mined coal filled composites exhibited pronounced decrease of impact strength. For filled polyethylene the notched impact strength value for the B type coal samples was approx. 22% higher than for the A type coal samples. The degree of impact strength decrease for composites with both types of mined coal was similar. It was impossible to compare values for filled and unfilled polyethylene because even notch samples of unfilled polyethylene did not break. For polyamide filled with both types of mined coal notched impact strength results were similar.

Observed impact strength decrease was very high and reached about 80% of initial values. Impact strength results confirm that composites became less deformable and more brittle after mined coal particles incorporation. Once more deteriorating influence of coal was more significant for polyamide composites than for polyethylene composites. Achieved results are typical for polymers filled with inactive particles. Also impact strength can be enhanced by appropriate fillers surface modification, for example by free surface energy changes or by coupling agents application.

Results of hardness measurements show that increase of coal content was accompanied by higher hardness (see Fig. 5). The higher was hard coal particles content the higher was composite hardness. It is the obvious result of higher hardness of coal particles than of polymer matrix. This effect is observed for all composites with fillers harder then matrix. Observed increase for polyethylene with highest coal content composites was about 25% and for polyamide composites was only about 10%. It is the consequence of smaller hardness difference between matrix and filler in the cas of polyamide composites than in the polyethylene composites. Hardness of polyamide composites was much higher then polyethylene composites. It is natural result of higher hardness of polyamide matrix. For polyethylene hardness of the B type coal composites was slightly higher than hardness of the A type coal composites. For polyamide results were quite in the opposite. Positive aspect of higher hardness is that usually higher composite hardness is accompanied by higher resistance to wear but this principle is not fulfilled in all cases. Additional research of this problem is needed and is planned. Research of friction coefficient is also planned.

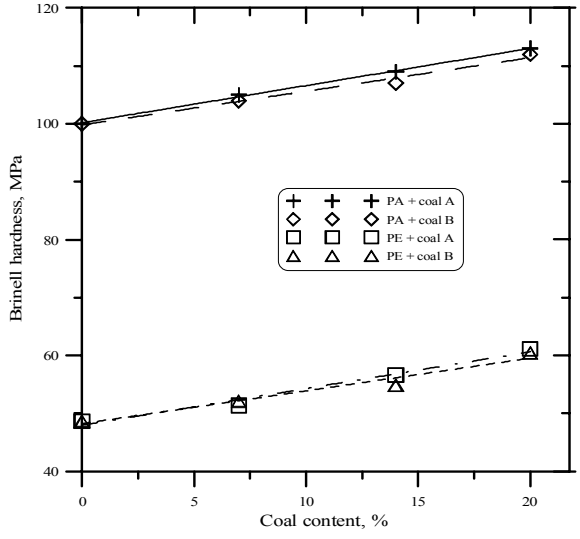

Fig. 5. Dependences of ball hardness of polyethylene and polyamide composites on mined coal content

Taking into account all achieved results on influence of mined coal on mechanical properties of polyethylene and polyamide one can says that changes caused by coal introduction into these polymers are similar to those obtained for a number of typical inactive mineral fillers without surface modification or coupling

agents application. Significant decrease of tensile strength, elongation at break and impact strength values shows that low adhesion forces between filler's particles surface and polymer matrix took place. Polymer matrix – filler interfaces were not able to transmit internal stresses and were places where cracks were easily formed and easily propagated. It is understandable taking into account that no filler's surface modification was performed on this stage of research. Higher affinity of polyethylene to coal than polyamide to coal caused that negative changes for polyethylene composites were lower than for polyamide composites In further research application of coupling agents and surfactants is planned.

Results of surface resistivity tests show that mined coal fine particles decrease electrical resistance of polyamide and polyethylene. Dependences of surface resistivity on coal particles content are shown in Fig.6. Relative surface resistivity decrease was at the same level for polyamide compounds and polyethylene compounds. For polyamide filled with highest content of hard coal about 40% surface resistivity decrease was observed. For polyamide filled in the same level with anthracite measured surface resistivity decrease was about 46%. Polyethylene composites exhibited for both types of coal similar surface resisitvity decrease about 45%. Obtained results are fully understood taking into account that coal is known as good electric conductor. Decrease of electric resistance due to mined coal introduction into polymer matrix opens for these composites many interesting fields of application where low surface resistivity is demanded. Low surface resistivity is also one of properties demanded of materials with low tendency to electrification. It is very important for all application where explosion danger exists for example in mining industry. `Also through resistivity is expected to decrease but it was not measured. Mined coal is much cheaper that other fillers applied for this purpose

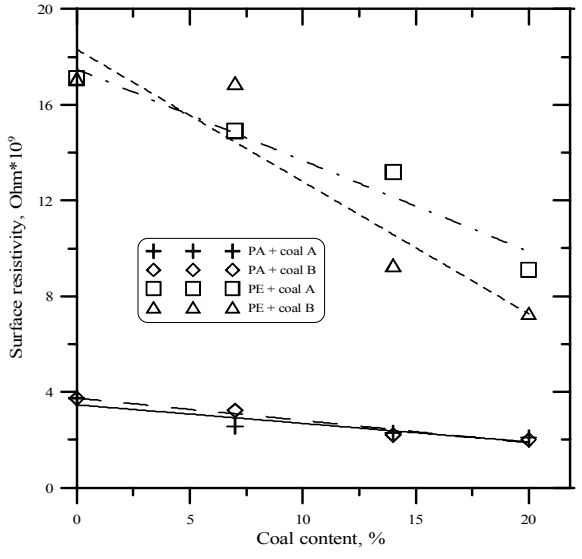

Fig. 6. Dependences of surface resistivity on mined coal content for polyethylene and polyamide composites

4. Conclusions

All investigated composites properties were changed as a result of introduction of mined coal fine particles into polyethylene and polyamide matrixes. For all researched characteristic influence of mined coal on polyamide was greater than on polyethylene.

Tensile strength, elongation at break and impact strength substantially decreased as a result of mined coal addition to polyethylene and polyamide. Increase of Brinell ball hardness was simultaneously observed. Changes of mechanical properties caused by introduction of coal are similar to those obtained for a number of typical mineral fillers without surface modification.

Surface resestivity results open very interesting fields of applications of investigated materials where low surface resistivity is demanded. Introduction of anthracite mined coal (type B coal) into thermoplastic polymers gave better results than introduction of hard mined coal (type A coal).

Obtained results show that poor adhesion between polymer matrixes and mined coal particles was achieved. Application of coupling agents and surfactants can probably improve adhesion and in this way many composites properties. Additional research of this problem is planned.

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