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Reinforced plastics based on polypropylene and dressed basalt fibers

Abstract: *The use of [(alkoxy)(acrylatoxy)titanoxy] boranes as dressings for basalt fibers applied as reinforcing fillers in polypropylene has been studied. The [(alkoxy)(acrylatoxy)titanoxy] boranes under study were of different structures and with a varying number of acrylatoxy groups in the molecules of the compounds. It has been shown that the compounds whose molecules have both reactive butoxy and acrylatoxy groups at the titanium atom in an amount of 0.75–1.00 wt. % of the fibrous filler will provide basalt plastics with higher strength properties. Also, the complex-forming atoms (titanium and boron) exhibit an additional network of coordination bonds with the oxygen in the products of polypropylene oxidation. The combination of these two factors enabled obtaining basalt plastics having tensile strength as high as 83.0 MPa.*

Keywords: *polypropylene, impregnation, composite.*

NAPEŁNIANIE TWORZYW OPARTYCH NA POLIPROPYLENIE I WŁÓKNACH BAZALTOWYCH

Streszczenie: *W pracy badano apreturę włókien bazaltowych, jako napełniacza wzmacniającego polipropylenu. W badaniach wykorzystano [(alkoksy)(akryloksy)tytanoksy] boran, które miały różną strukturę i różną liczbę grup akrylanoksylowych w cząsteczkach związków. Wykazano, że związki, w których cząsteczki miały zarówno butoksylowe i akryloksylowe reaktywne grupy w pobliżu atomu tytanu w ilości od 0,75 do 1,0 % wag. napełniacza włóknistego zapewniają uzyskanie tworzyw bazaltowych o lepszych właściwościach wytrzymałościowych. Ponadto, atomy kompleksotwórcze (tytanu i boru) wykazują dodatkową sieć wiązań koordynacyjnych z tlenem w produktach utleniania polipropylenu. Połączenie tych dwóch czynników powoduje uzyskanie tworzyw bazaltowych mających wytrzymałość na rozciąganie wynoszącą nawet 83,0 MPa.*

Słowa kluczowe: *polipropylen, impregnacja, kompozyt.*

1. INTRODUCTION

In the last few decades, thermoplastics have been increasingly used in various industries due to a whole range of valuable properties, such as high strength, chemical stability, high thermal and electrical insulating properties, the ability to easily form products of complex shapes on the high-performance equipment, and reliability of the operation [1, 2]. Still more important for industries are composite materials based on them, especially thermoplastics reinforced with fibrous fillers including basalt fibers [3]. Fibrous fillers introduced to a composite polymeric material can significantly increase its strength,

toughness, reduce cold flow, and improve its thermal stability. Through the contact surface, the polymer matrix evenly distributes mechanical loads onto the fibrous filler, creating conditions for them both to work as monolith. If the fibers have higher strength than the thermoplastic itself, the former provide the composite material with higher strength, toughness, hardness, thermal stability and other physical and mechanical properties essential for further performance.

The previous research on the development of antifriction-purpose polypropylene-based basalt plastics showed the advantages of reinforcing the thermoplastics with basalt fibers [4, 5]. This gave a 51% increase in the strength characteristics

of new composites, a 27% increase in Charpy impact strength and an 11°C improvement of Vick thermal stability, which provided a better performance of the new-type basalt plastics under heavy power loads.

It was interesting to carry out a research on the use of basalt fibers pre-dressed with bortitan alkoxy- and bortitan(alkoxy)(acrylatoxy)-containing compounds of various structures in these polypropylene-based composites, and to trace the influence of the amount and nature of a dressing on the physical and mechanical properties of the composites.

Polypropylene, which today is being produced on a large scale [6–8], is a thermoplastic linear polymer having an isotactic structure with regular spatial helix chain (each repeating unit of the polymer chain contains three monomer units) and a degree of crystallinity up to 72–75%. Injection molding is used to process it into machine parts, household products, containers for storage and transportation of bulk cargoes, and hollow ware for liquids. It is also processed by extrusion molding in case of films, sheets, pipes, profiles, and fibers. Although polypropylene is characterized by rather high physical and mechanical properties (tensile strength of 30–35 MPa, Vick thermal stability of 145–155°C), the technical progress requires new and better structural materials with an improved set of physical and mechanical properties, which are capable of working in a wide range of power loads, temperatures, environments, as well as new stronger composite materials, including those based on polypropylene.

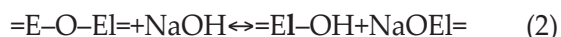
2. EXPERIMENTAL

Polypropylene PP Tatren HT 30, produced by Slovnaft Petrochemicals in Slovakia was used as a polymer matrix. It was modified by polyamide 6 amounting to 4 wt. % content of the polymer matrix. Chopped basalt fibers made of O330 jute (TU U 00292729001–96) were used as filler. They were prepared by a short-time pre-treatment with an alkali solution as

described in [9]. This pre-treatment will both remove lubricant from the fiber surfaces and activate the surface layers of fibers due to their reaction with the alkali solution as follows:



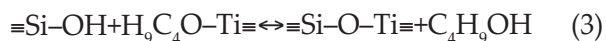
or:



(where El = Fe, Al, Mg, Mn, etc.)

Groups = El-ONa or $\equiv\text{SiONa}$ formed on the surface of the fibers are highly polar groups and are able to enhance the cohesive interactions at the interface in the “polymer matrix – fiber” system.

Groups $\equiv\text{SiOH}$ or = El-OH are potential agents for transesterification of butoxy groups at the titanium atom of a dressing, which causes the formation of chemical bonds between the dressing and the filler as shown below:



In addition, fiber surface treatment with an alkali solution causes micro asperities on its surface, which increase the surface area of physical contacts between the polymer matrix and fibers and, consequently, the strength of physical interactions between them.

The fibers were dressed by 5 wt. % solution of each dressing in butyl alcohol. The content of compounds adsorbed on the fibers was changed from 0 to 1.25 wt. % in 0.25 wt. % increments.

Physical and mechanical properties of the basalt plastic samples obtained experimentally were evaluated according to the current standards within 24 hours after the manufacture. The Table shows the structural formula of dressings used for basalt fibers, i.e. butoxy esters of orthotitanic acid, tris[tri(butoxy)titanoxy] borane and relevant acrylate substituted groups based on it. The synthesis [(butoxy)titanoxy] boranes was carried out accordingly [10]. It is known that

alkoxyorthotitanates found wide application as adhesion promoters of pigments and fillers [11], polymerization in solution [12], primers [13].

3. RESULTS AND DISCUSSION

At the first stage of the research, the relationships between the adhesion strength in the “polypropylene – basalt fiber” system and the amounts and nature of a dressing adsorbed on the fibers were studied.

The dependences of the adhesive strength in the “polypropylene – basalt fiber” system on the concentrations and nature of the dressings were evaluated through the direct method according to [14]. The experimental data shown in Fig. 1 reveal a clear picture of the expected mechanical properties of the obtained basalt plastics.

Figure 1 shows that the highest values of adhesive strength in the studied system are achieved in all the cases where the concentration of the dressing on the fibers is between 0.50 and 1.00 wt. % (with a maximum at 0.75 wt. %). A further increase in the amount of dressing will not increase the adhesive strengths, but will rather cause their gradual decrease. However, the value of adhesive strength greatly depends

on the nature of the dressing used. Its lowest value (7.2 MPa) is typical of Compound 1 (tetrabutoxytitan). Introduction of a boron atom into the structure of butoxy-derivative ether of orthotitanic acid (Compound 2, Table) gives an increase in the adhesive strength up to 7.8 MPa. If butoxy groups in the structure of Compound 2 are partly substituted for the remainder of the acrylic acid, it will cause even higher increase in the adhesion strengths (up to 8.6; 10.8; 11.5 MPa in the series of Compounds 3, 4, 5, Table) in accordance with the number of butoxy groups substituted for the remainder of acrylic acid.

Thus, we can conclude that the introduction of a boron atom into a tetrabutoxytitan molecule (Compound 1, Table) causes an increase in the adhesive interaction at the „basalt fiber – polypropylene” interface due to the fact that a boron atom, similar to a titanium atom, is capable of coordination interactions with electron acceptor atoms. A simultaneous substitution of the donor butoxy groups at the titanium atom in Compounds 3–5 for the remaining unsaturated acceptor acrylic acid will further increase the strength of adhesive intermolecular interactions.

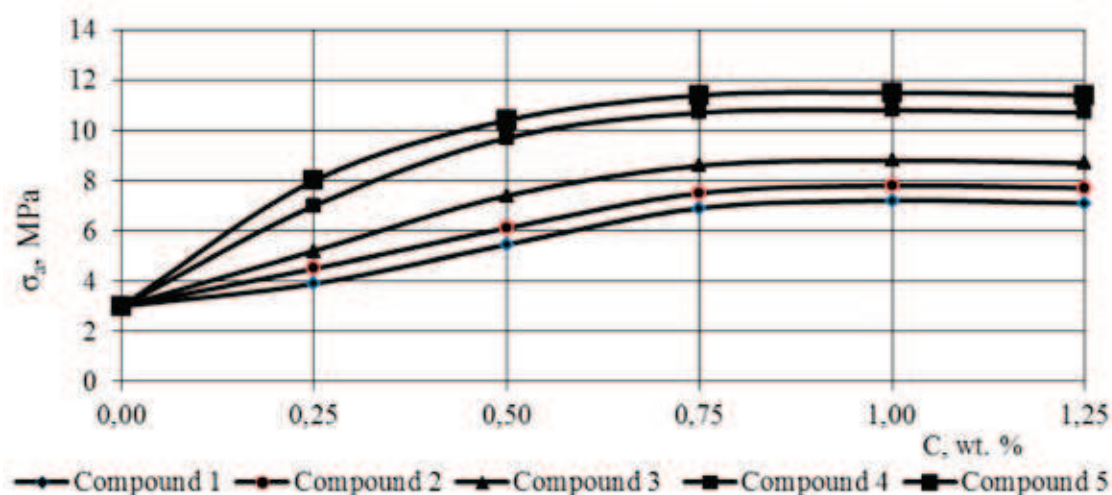


Figure 1. Dependence of adhesive strength in the „polypropylene – basalt fiber” system on the dressing concentrations on the fibers; notation as in Table

Rysunek 1. Zależność wytrzymałości adhezyjnej, w układzie polipropylen – włókno bazaltowe, w zależności od ilości użytego impregnatu; oznaczenia jak w tabeli

Table. Properties of the experimental samples of polypropylene-based basalt plastics as dependent on the dressing amount and structure

Tabela. Właściwości bazaltowych próbek doświadczalnych na bazie polipropylenu w zależności od struktury i ilości impregnatu

Structural formula of dressing	Properties	Amount of dressing on fibers, wt. %				
		0,00	0,25	0,50	0,75	1,00
Ti(OC ₄ H ₉) ₄ (Compound 1)	melt flow rate, g/10 min	2,00	1,56	1,34	1,23	1,12
	tensile strength, MPa	40,7	43,6	49,8	52,0	50,1
	tensile elongation, %	92	104	112	138	128
	Charpy tensile strength, kJ/m ²	44,9	50,1	55,2	59,3	56,4
	Vick thermal stability, °C	160	162	165	169	167
B[OTi(OC ₄ H ₉) ₃] ₃ (Compound 2)	melt flow index, g/10 min	2,00	1,70	1,53	1,20	1,05
	tensile strength, MPa	40,7	47,0	52,9	55,6	53,0
	tensile elongation, %	92	102	116	130	124
	Charpy tensile strength, kJ/m ²	44,9	55,1	60,2	64,3	51,2
	Vick thermal stability, °C	160	162	167	170	168
B ₂ { [OTi(OC ₄ H ₉) ₃] ₂ [OTi(OC ₄ H ₉) ₃] ₂ -(OOCCH=CH ₂) }	melt flow index, g/10 min	2,00	1,60	1,32	1,14	1,02
	tensile strength, MPa	40,7	44,6	51,2	59,0	57,0
	tensile elongation, %	92	97	112	124	120
	Charpy tensile strength, kJ/m ²	44,9	53,0	55,0	57,4	57,2
	Vick thermal stability, °C	160	165	170	174	168
B ₂ { [OTi(OC ₄ H ₉) ₃] [OTi(OC ₄ H ₉) ₃] ₂ -(OOCCH=CH ₂) ₂ }	melt flow index, g/10 min	2,00	1,74	1,46	1,20	1,12
	tensile strength, MPa	40,7	46,0	56,0	67,3	62,0
	tensile elongation, %	92	94	108	126	120
	Charpy tensile strength, kJ/m ²	44,9	53,0	55,0	58,1	55,2
	Vick thermal stability, °C	160	163	169	172	168
B-[OTi(OC ₄ H ₉) ₂ -(OOCCH=CH ₂) ₃] ₃ (Compound 5)	melt flow index, g/10 min	2,00	1,50	1,32	1,09	0,98
	tensile strength, MPa	40,7	52,0	65,2	83,0	72,3
	tensile elongation, %	92	98	116	128	124
	Charpy tensile strength, kJ/m ²	44,9	55,1	57,2	61,3	59,2
	Vick thermal stability, °C	160	163	169	173	167

It is likely that these reactions and additional coordination interactions will also be manifested in the properties of newly developed polypropylene-based basalt plastics; they will facilitate the production of stronger composite materials, with longer service life under extreme conditions of operation.

At the second stage of the studies, polypropylene-based basalt plastics were

obtained using basalt fibers pre-dressed with Compounds 1–5 by the common method [4]. Their properties were analyzed to reveal the dependences on the amount and nature of the fiber dressing (Table and Fig. 2).

Analyzing the influence of structures of the used dressings (provided that they are applied in equal weights) on the properties of the obtained polypropylene-based basalt plastics, we can see

that in each case, the change in the properties after a dressing is applied onto the fibers is of an extreme nature, similar to that exhibited in the previous experiments. The highest values are in each case achieved with the dressing amounts of about 0.75 wt. %. However, a series of dressings using Compounds 1–2 that structurally have a single type of reactive groups (butoxy groups) at the titanium atom, exhibit higher performance properties of composites (tensile strength, Vick thermal stability, Charpy impact strength) with Compound 2 than with Compound 1 (tetrabutoxytitan); this is obviously related with the introduction of an additional complex-forming atom (boron) into the molecule (Compound 2). This effect can be explained by better coordination interactions in the “polypropylene – basalt fiber” system due to the presence of the additional complex-forming atom of boron.

3–5) in the starting tris[tri (butoxy)titanoxy] borane by a reaction of transesterification. The study reveals an extreme nature of changes in the sample properties in all the cases; the highest values were achieved when using the dressing in an amount of 0.75 wt. % (similar to the previously discussed results for Compounds 1 and 2, Table). At the same time, with an increased number of polar acrylate residues at the titanium atom in the compound (dressing) structure, the absolute values increase and reach their maximum when using Compound 5 (tensile strength of 83.6 MPa; Vick thermal stability of 173°C; Charpy impact strength of 61.3 kJ/m²), which is 204, 137 and 8%, respectively, higher than in basalt plastics reinforced by undressed fibers.

Given that no radical initiators were introduced into the dressing solution (Compounds 3–5, Table), and the dressing had nothing for acrylate groups to copolymerize with, then the results

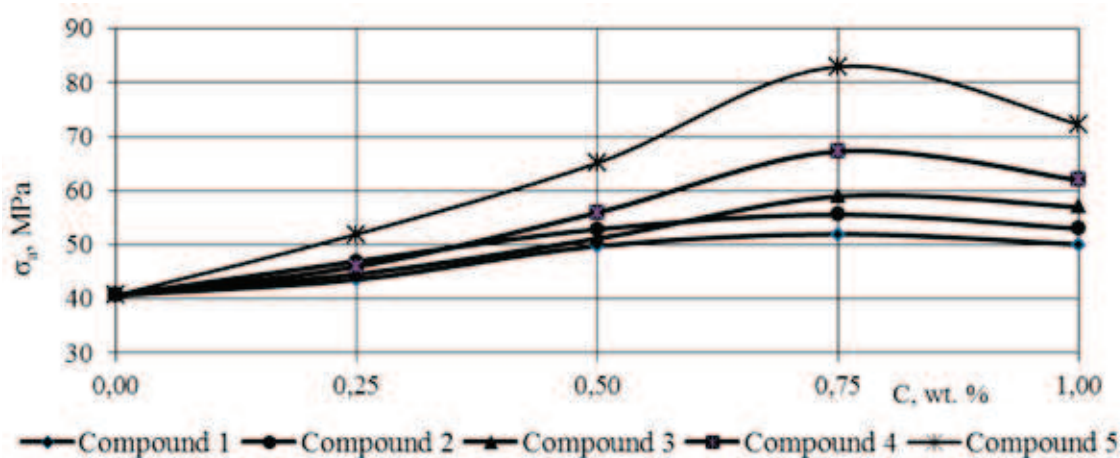


Figure 2. Strength characteristics of basalt plastics as dependent on the concentration and nature of the fiber dressing; notation as in Table

Rysunek 2. Charakterystyka wytrzymałościowa tworzyw bazaltowych w zależności od ilości i rodzaju impregnatu; oznaczenia jak w tabeli

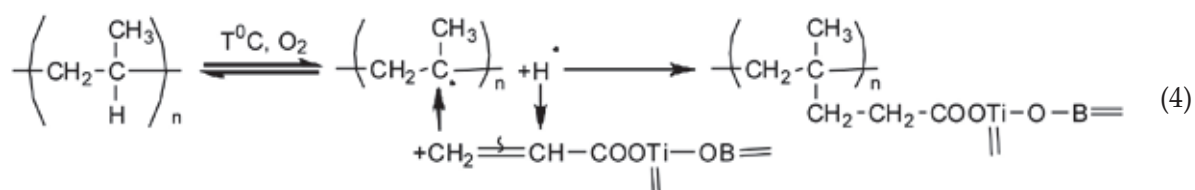
The properties of the experimental samples of basalt plastics based on series 2–5 dressings were studied. As a variable factor, they had butoxy groups (Compound 2, Table) at the titanium atom or both butoxy groups and different amounts of polar acrylate groups obtained by prior substitution of butoxy groups for the corresponding acrylate groups (Compounds

may be explained as follows: every other carbon atom in the main chain of polypropylene is a tertiary one, so hydrogen at it may be the easiest to undergo oxidative processes, especially at temperatures above 100°C. Air oxidation is accompanied by a decrease in the molecular weight of a polymer, increased elongation, and degradation of other characteristics, as well as

formation of peroxide, hydroxyl, acid, aldehyde and other functional groups and free radicals in the degradation products. At the same time, the polypropylene undergoes degradation through another mechanism, which is accompanied by removing a proton from the tertiary carbon atom. This can evoke an addition reaction with a further modification of polypropylene macromolecules in the presence of unsaturated compounds (e.g. acrylic acid).

Although oxidation reactions evoked by radicals generated by the air oxygen proceed much more slowly in the absence of radical initiators, the modification of polypropylene by an addition of polar unsaturated monomers (acrylonitrile, styrene and others) have long been used [8].

Thus, we can assume that in the injection molding of polypropylene-based composite samples, the following reaction will take place (4):



This ensures the dressing binding with the polymer matrix. Moreover, in the prior studies, butoxy groups at the titanium atom caused reactions with the filler. The number of these reactions will depend greatly on the temperature and time of the material heating under pressure. In addition, atoms of boron and titanium in the dressing structures contribute to improving the physical and mechanical properties of the test samples of obtained basalt plastics; these atoms implement coordination interactions with oxygen atoms in the degradation products that form in the oxidation of polar functional groups and on the filler surface; these coordination interactions are known to be as strong as σ -bonds. All the above chemical reactions and interactions that simultaneously occur in a polypropylene

composition during an injection molding at 210–230°C, contribute to the total positive effect manifested in an improvement of physical and mechanical properties of basalt plastics (Fig. 2).

4. CONCLUSIONS

Thus, to summarize the above, we can state that:

- the use of dressing series under study for pre-dressing basalt fibers shows good prospects for a substantial increase in physical and mechanical properties of new type basalt plastics based on polypropylene;
- the highest values of physical and mechanical properties in basalt plastics may be achieved when the investigated series of dressings is applied onto the fibers in the amount of 0.75–1.00 wt. %. In addition, the use of tris[di(butoxy)(acrylatoxy)titanoxy] borane may result in approximately 2 times increase in the mechanical properties;

- further increase in the amount of dressing on basalt fibers is inexpedient, since it leads to the drop in the physical and mechanical properties of polypropylene-based basalt plastics;
- since Ukraine has a well-established raw material base for the production of both polypropylene and basalt fibers, the above basalt plastics have every reason to be competitive in the market of high-strength and low specific weight materials, especially in the aircraft, rocket, automobile production and other industries.

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