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Adhesive and impact strength of hybrid layered metal-polymer composites reinforced by basalt fiber

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This work shows the possibility of obtaining hybrid layered metal-polymer composites based on low-carbon steel and aluminum alloys with interlayers of basalt fiber reinforced thermoplastic polymer — polyetheretherketone by methods of hot and cold bonding with the use of hot and cold curing adhesives, respectively. The adhesive tear and shear strength of composites obtained by two alternative methods and the impact strength of steel-polymer and aluminum alloy-polymer joints were evaluated. The tests of five-layered composites for impact bending on samples with "crack-arrester" type V-notch (with the orientation of the notch line across the composite layers) at temperatures of −60, +20, and +200°C were carried out. The analysis of the test results showed that the composites have increased strength at shear loads and resistance to brittle fracture at low climatic and high working temperatures. Fractographic analysis of the fracture surface of composites allowed to determine that the fracture proceeds through adhesive, cohesive, and mixed mechanisms. Cohesive fracture is initiated in the polymer layer by nucleation and crack growth along the fiber-matrix interface, as well as cracking of the basalt fibers.

Keywords: layered metal- polymer composite, hot pressing, cold bonding, impact strength, adhesive strength.

1. Introduction

The development of new equipment and technologies requires the design of new materials with superior physical, mechanical and functional properties [1]. In particular, the development of ultralight composites for structural and functional applications is the actual task of modern aerospace and automotive industries. Currently, all ways to improve the performance properties of light metals and alloys, including doping, severe plastic deformation and heat treatment, have been practically exhausted. It is possible to give materials new unique properties by combining different materials in a single composition. However, combining different metals and alloys or reinforcing them with ceramic disperse particles in composite material development does not practically solve one of the main tasks of modern materials science — significant reduction of specific weight of metal structure [2]. Combining metallic materials of high strength and stiffness with low-density polymeric materials allows obtaining a fairly lightweight composite material with improved strength properties [3–5]. Layered composites are widespread today due to the possibility of joining metallic and polymeric materials using adhesives by traditional molding — vacuum-autoclave, vacuum-furnace, press molding. Application of thermoplastic polymers with the possibility for multiple recycling and consequent reduction of consumption of thermosetting polymers of one production cycle is important from the point of view of ecology and nature preservation [6]. The All-Russian Scientific Research Institute of Aviation Materials has developed layered metal-polymer composites based on aluminum alloy with interlayers of filled polymeric materials, successfully implemented in the structural elements of the AN-124-100 cargo aircraft [7]. The application of these composites allowed to decrease significantly the growth of fatigue cracks due to the features of the material structure and 5–20 times increase of the operational reliability of the aircraft aggregates reducing the weight of the aggregates by 12%. In the railway industry, there are also new tendencies related to the use of aluminum alloys and composite materials in the construction of the passenger car bodies. In Switzerland, Japan and Germany the share of cars made of aluminum alloys of Al-Mg-Si system has reached 80%. In Russia, there is just beginning of serial production of train made of aluminum alloys [8]. Reducing the weight of the structure is the main requirement for increasing the speed characteristics of trains. In this regard, the development and implementation of metal-polymer composite is an important and necessary requirement for designing new high-speed rail transport. Earlier works [9,10] have shown that layered metal-polymer composites based on steels, aluminum alloys and rubber can be used as elements of shock absorbers for high-speed rail transport due to their high damping properties, resistance to brittle and fatigue failure. To evaluate the influence of technology, type of adhesive and compositions of layered metal-polymer composites used for railway transport, studies were continued on composites based on steels, aluminum alloys and reinforced thermoplastic polymer. The aim of this work was to study the adhesive and impact strength of a hybrid layered metal-polymer composite based on Fe-2Mn-Si steel, Al-Mg3 alloy and thermoplastic polymer — polyetheretherketone (PEEK) reinforced by unidirectional basalt fibers and to investigate the fractographic features of their fracture under impact and static loads in order to assess the possibility of application these composites in the structures of passenger and freight cars of a new generation.

2. Experimental procedure

2.1. Materials and fabrication of composites

The objects of the study were three- and five-layered metal-polymer composites based on metal layers with interlayers of a filled polymer composite. The metal layers used were low-carbon low-alloy Fe-2Mn-Si steel and wrought Al-Mg3 alloy. The constituent metal composites of the material had the following chemical composition (in wt.%): Fe-2Mn-Si steel (Fe (main), 0.12%C, 1.32%Mn, 0.68%Si, 0.12%Cu, 0.07%Cr, 0.07%Ni, 0.04%Al, 0.02%P, 0.01%S, 0.01%Mo); 001% steel (Fe (main), 0.0056%C, 0.123%Mn, 0.055%Nb, 0.053%Al, 0.044%Ti, 0.023%Si, 0.006%P, 0.004%S); Al-Mg3 alloy (Al (main), 3.4%Mg 0.6%Si, 0.5%Cu, 0.4%Mn, 0.05%Cr, 0.2%Zn, 0.1%Fe, 0.1%Ti). In the composition of layered package Al-Mg3 alloy and steel tapes were used in the hot-rolled and heat-treated (after hardening and high tempering) states, respectively. An optical emission spectrometer SPECTROMAXx was used to determine the chemical composition of the materials.

The polymer layers of the composites were made based on thermoplastic matrix polymer polyetheretherketone (PEEK) reinforced with 40 vol.% unidirectional basalt fibers. One of the advantages of PEEK in addition to low specific density is the possibility of its use as a substitute for metals due to high strength, corrosion resistance, low flammability [11,12]. The polymer matrix was filled with basalt unidirectional continuous fiber of 40 vol.% to increase the strength properties and impact toughness of the polymer matrix.

The fabrication of reinforced polymer composites was carried out in the Institute of Physics of Strength and Material Science of Siberian Branch of the Russian Academy of Sciences. The composite production technology consisted of 6 layers of PEEK film 250 μm thick by Victrex (UK) and 5 layers of unidirectional basalt fiber (Russia). After laying in the mold samples of composites based on PEEK were obtained by hot pressing on hydraulic press GOTECH GT-7014-A, at a pressure of 10 MPa and temperature of 400°C with a subsequent cooling rate of 2°C/min. At the end of the pressing process, the obtained billets were 75 × 65 × 2 mm in size. Polymer layers of composites were cut from the finished plates according to the billet size for tear, shear, impact and cyclic bending tests.

Layered metal-polymer composites were made using the technology of cold and hot bonding (hot pressing) with cold and hot curing adhesives, respectively. When obtaining composites by a cold method metal and polymeric layers were preliminary processed by an abrasive for formation of the developed rough surface of connection and degreased, then on a surface of plates the priming and base layers of heat-resistant glue VK-9 with the subsequent assembly of a package and its fixing within 24 hours were applied.

When obtaining composites by hot pressing the heat-resistant glue VS-10T was used. Preparation of the initial layers of the composite also included operations of grinding and degreasing. Manufacturing three- and five-layer composites was performed on a hydraulic press with a built-in heating device for 2 hours at a temperature corresponding to the adhesive curing temperature of 180 ± 5°C followed by cooling under pressure to 40°C. In the pressing process, four composite structures were obtained in which steel and/or aluminum plates were used as outer and central layers, respectively, and the intermediate layers were made of reinforced polymer (Fig. 1).

Thus, by hot pressing and cold bonding, hybrid composites characterized by a layered structure on the macro- and microscale were obtained. Composites are a five-layer structure of metal and polymer composite layers (Fig. 2 a), the latter consisting of alternating 6 layers of polymer and 5 layers of basalt fiber (Fig. 2 b).

2.2 Investigation of mechanical properties and structure

The study of adhesion strength of composites was conducted by shear tests according to GOST 14759-69 and tear tests according to GOST 209-75 using a test machine Zwick/Roell Z 2.5. The tested samples had a three-layered structure of the metal-PEEK/basalt-metal type in accordance with the geometry and dimensions regulated by the standards. The production of tested samples was carried out by cold and hot bonding.

Tests on the resistance of composites to brittle fracture were carried out according to GOST 9454-78 on a pendulum-type impact test machine IT 542M Tinius Olsen with a maximum stored energy of 543.7 J and the scale spacing of 1 J on samples 10 × 10 × 55 mm with a "crack-arrester" type V-notch (with the notch line across the layers of the composite) at temperatures of −60, +20 and +200°C. (Fig. 2 a). The test temperatures were chosen by taking into account the working temperatures of BK-9 and VS-10T and the polymer composite. A NEOPHOT 21 optical microscope was used to study the structure of the obtained composites. Fractographic analysis of the composite fracture surface after mechanical tests was carried out on a TESCAN VEGA II XMU scanning electron microscope.

3. Results and discussion

The microstructure of polymer composites in layered composites produced by hot pressing is shown in Fig. 3. As can be seen in Fig. 3 b, the polymer layers have a certain amount of porosity. In this case, the layers of basalt fiber are sufficiently well impregnated with a polymer binder. At the boundary of polymer and metal layers, there is an adhesion layer up to 100 μm thick, characterized by the presence of elongated pores from 25 to 300 μm. When studying the fracture pattern of the impact specimens using scanning electron microscopy, the presence of air pores up to 300 μm

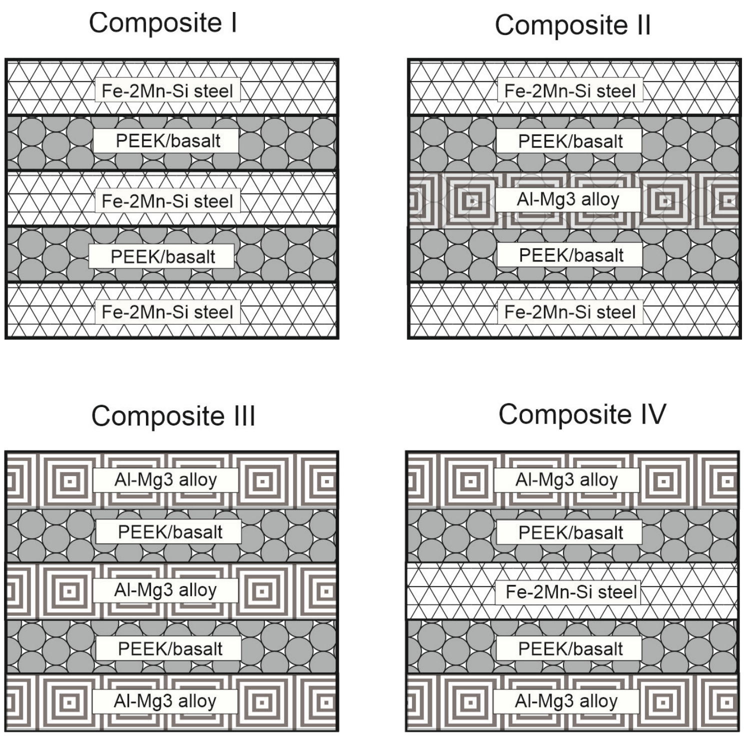
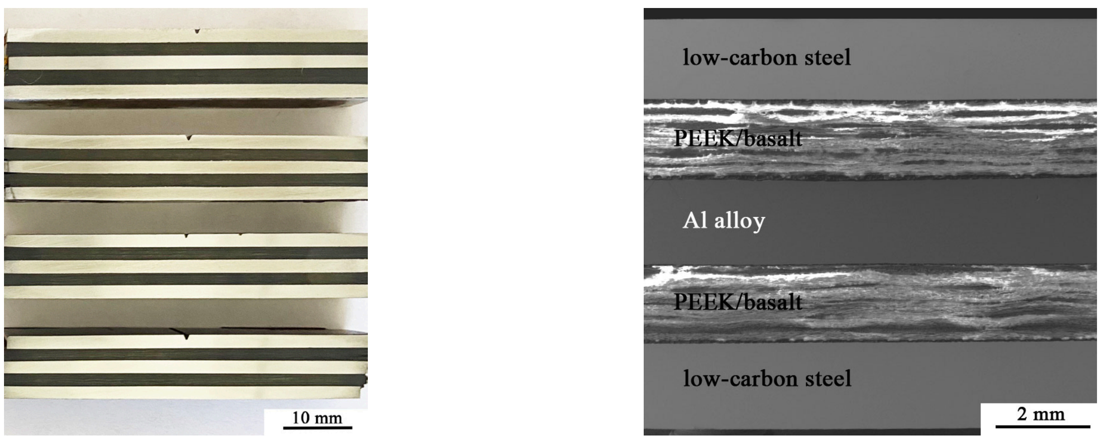
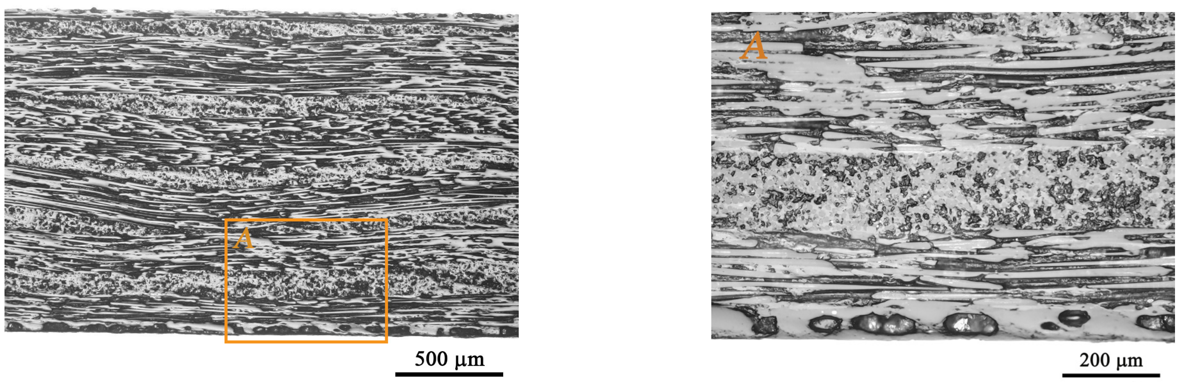


Fig. 1. Designs of layered metal-polymer composites obtained by hot pressing: Composite I — steel - PEEK/basalt - steel - PEEK/basalt-steel; Composite II — steel - PEEK/basalt - Al alloy - PEEK/basalt - steel; Composite III — Al alloy - PEEK/basalt-Al alloy - PEEK/basalt - Al alloy; Composite IV — Al alloy - PEEK/basalt - steel - PEEK/basalt - Al alloy.



a b

Fig. 2. Optical image of layered metal-polymer Composites I – IV (a) and SEM image of Composite II (b).



a b

Fig. 3. Microstructure of basalt fiber-reinforced polymer layer (a), and its fragment A at higher magnification (b).

is confirmed in the adhesion layer (Fig. 3). The presence of pores in the contact zone of the layers is undesirable due to the occurrence of additional stress concentrations at the interlayer boundary and the probability of the crack origin and development. The appearance of pores in the adhesive layer is due to the bond formation in the air. This problem is solved by vacuuming the process of obtaining an adhesive joint. That is confirmed in the work [13] in which strength increase of the joint by more than 20% was achieved by switching to the vacuum bagging technique.

The test results of composite samples for tearing and shear showed that the adhesion strength of composites obtained by hot pressing is higher than that of composites obtained by cold bonding. The data of shear tests of composites demonstrated the opposite behavior: the adhesion strength of composites obtained by cold bonding is higher than that of composites processed by hot pressing (Table 1). Regardless of the type of composite production, higher σ_u values are observed for steel - PEEK/basalt compounds than for Al alloy - PEEK/basalt compounds. This is due to the inevitable presence of oxide films on the surface of metal layers before the application of the adhesion layer. Fe_3O_4 film on the surface of steel layers has an activating effect and contribute to the formation of a strong bond, while the Al_2O_3 film on the contrary has a passive effect [14].

Since the results of the tear tests demonstrated higher adhesive strength of the adhesive joints of composites obtained by hot pressing, the impact tests were carried out exclusively on the samples of composites made by this technology. According to the results of impact bending tests, it was found that the highest values of impact strength were obtained on Composite I based on steel layers, and the lowest values of impact — on Composite III based on aluminum layers. It is noted that the fixed values of impact strength of composites are lower than the KCV values of its original components: Al-Mg3 alloy ($KCV_{+20°C}$ = 0.25 MJ/m^2) and Fe-2Mn-Si steel ($KCV_{+20°C}$ = 0.85 MJ/m^2). However, it is important to mention that composites do not break down completely. No more than two layers of the composite fracture in the direction of the impact load. After that, there is a crack arrest on the interface, a sharp change in the trajectory of the crack and its further growth along the interface with the appearance of composite delamination (Fig. 4). Composites III based on aluminum layers have similar values of impact strength at −60, +20, +200°C test temperatures (Table 2). One can note an increase in the impact strength with a decrease in the temperature from 200 to −60°C for other composites structures. A decrease in the impact strength with decreasing temperature is typical of metallic materials. But this regularity is not observed in layered metallic structures with "crack-arrester" layer orientation. The increasing tendency of the impact strength of layered composites at lower temperatures is associated with the manifestation of the "delamination toughness" effect when the increase in impact strength mostly results from an increase in the extent of delamination in the composite. This effect is also observed on layered metallic and metal-rubber composites, the test results of which are given in works [10,15]. Since the working temperatures of BC-10T adhesive are in the range of −60…+300°C, the low-temperature tests were carried out under critical conditions for the adhesive bond. Therefore, the impact load at −60°C led to delamination at almost all interfaces of the composites.

The polymer layers showed high resistance to brittle fracture during impact loading due to the layered structure formed by reinforcement with continuous basalt fibers [16,17]. Only one polymer layer in all composite structures was destroyed by the impact, but a developed network of microcracks along the basalt fibers was observed inside the polymer layers.

From the results obtained it has been found that a slight decrease in the weight of the steel - PEEK/basalt - steel - PEEK/basalt - steel (Composite I) type structure due to

Table 1. Results of composite tear and shear tests.

Technology	Composite connection	Adhesive strength σ_u, MPa	
		Tear	Shear
Cold bonding	Steel - PEEK/basalt - steel	3.2	16.7
	Al alloy - PEEK/basalt - steel	1.9	–
Hot pressing	Steel - PEEK/basalt - steel	4.7	11.3
	Al alloy - PEEK/basalt - steel	2.6	–

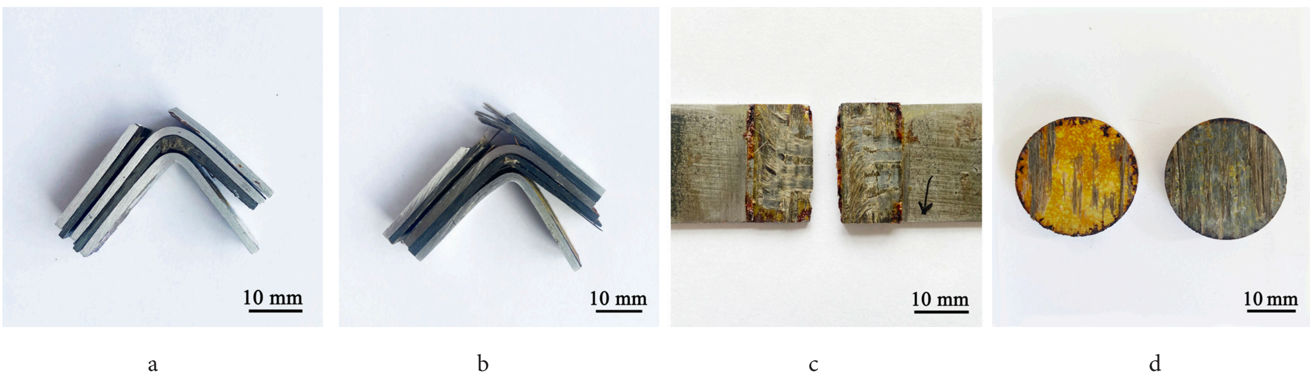


Fig. 4. (Color online) Macro-images of Composite III impact specimens at 20°C (a) and Composite IV at +200°C (b) and steel - PEEK/basalt - steel composites after shear (c) and tear tests (d).

a replacement of the central steel layer with aluminum (Composite II) leads to a noticeable, 1.3..1.6 times, decrease in the impact strength at temperatures −60…200°C. But the possibility of cost reduction of Al alloy - PEEK/basalt - Al alloy - PEEK/basalt - Al alloy (Composite III) type structure by replacing the central aluminum layer with a steel one (Composite IV) leads to an increase in the impact strength of the composite by a factor of 1.3…2.1. Strengthening of the structure with external steel layers while maintaining the central aluminum one (Composite II) also leads to an increase in the impact strength by a factor of 1.5…2.0. Thus, in order to increase the impact strength of the layered composite structure, it is more efficient to introduce a strengthener material as a central layer in a symmetrical composite package. It is in good agreement with the result of previous studies reported in [9,10].

When composites are tested for tearing, shear and impact bending, fracture occurs by adhesion, cohesion and mixed mechanisms. The adhesive fracture occurs at the interface between the metal layer and the adhesive. The cohesive fracture takes place along the polymer layer by developing a network of cracks at the interface between the basalt fiber and the matrix. The adhesive interaction at the interface between the fiber and PEEK is relatively weak due to the different polarity and absence of reactive functional groups on the PEEK, and the smooth fiber surface [18].

Analysis of SEM images of the fracture surface of the impact specimens showed that under the action of loading, cohesive fracture along the polymer layer occurred due to internal delamination along the fiber-polymer matrix interface when the stress corresponding to the adhesive strength of the system is reached. At the same time, cracking of the basalt fibers took place (Fig. 5b–c). As fibers break, new microcracks are initiated, the development of which leads to the formation of the main crack, leading to total failure [19,20].

This fracture type of PEEK/basalt layer is considered as a brittle one caused by the high content of hard filler [21]. At the same time, a high filler content provides strengthening of the thermoplastic matrix PEEK by stress transfer from the matrix to the filler and changing the direction of the crack growth at a contact with the solid filler.

4. Conclusions

The possibility of obtaining new layered composite materials based on low-carbon steels, aluminum alloy, and thermoplastic polymer reinforced with continuous basalt fiber by hot pressing with increased shear strength and resistance to brittle failure at low climatic and high working temperatures has been shown.

The results of tear and shear tests of metal-polymer composites showed that hot pressing with a hot-curing adhesive provides a stronger tensile bond, and the cold bonding method with a cold-curing adhesive gives a higher tear strength.

It was found that the steel - PEEK/basalt bond has a higher adhesion strength than the Al alloy - PEEK/basalt bond. The difference in the adhesive strength of these adhesive compounds is caused by the different influences of the Fe_3O_4

Table 2. Results of impact bending tests of five-layer metal-polymer composites at different test temperatures.

Material	Impact strength, KCV, MJ/m^2		
	−60°C	+20°C	+200°C
Composite I steel - PEEK/basalt - steel - PEEK/basalt - steel	> 0.55	> 0.52	> 0.47
Composite II steel - PEEK/basalt - Al alloy - PEEK/basalt - steel	> 0.41	> 0.38	> 0.30
Composite III Al alloy - PEEK/basalt - Al alloy - PEEK/basalt - Al alloy	> 0.21	> 0.20	> 0.20
Composite IV Al alloy - PEEK/basalt - steel - PEEK/basalt - Al alloy	> 0.45	> 0.33	> 0.25

Note: The KCV > sign means that all layers of the composite have not failed completely.

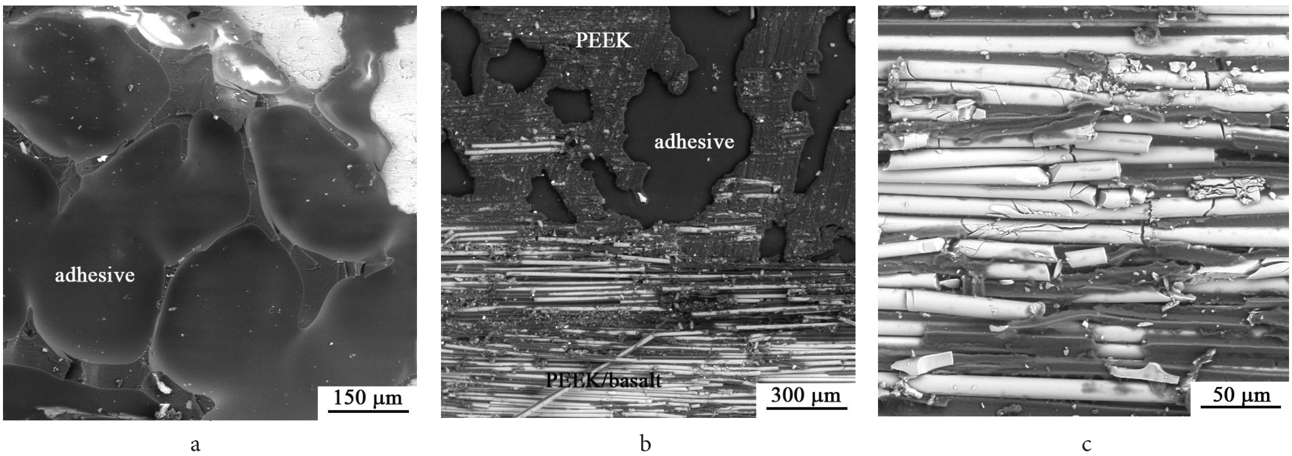


Fig. 5. SEM images of the fracture surface of Composite III impact specimens tested at −60°C.

and Al_2O_3 oxide films on the formation of a strong adhesive bond.

An abnormal increase in the impact toughness values of the studied composites with decreasing of test temperatures from +20 to −60°C, associated with the activation of the “delamination toughness” effect characteristic of layered materials, was revealed.

Composites break down by adhesive, cohesive, and mixed mechanisms. Cohesive fracture is initiated in the polymer layer by nucleation and crack growth along the fiber-matrix interface, as well as cracking of the basalt fibers.

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