Prediction of compatibility of polypropylene and modified basalt fibers

K B Galitseiskii¹, T A Matseevich² and A A Askadskii²,³

¹ Moscow aviation Institute (national research University) 125993, Moscow, Volokolamsk highway, 4
² Moscow State University of Civil Engineering, Yaroslavskoe shosse, 26, Moscow, 129337, Russia
³ A.N. Nesmeyanov Institute of organoelement compounds of Russian Academy of Sciences 119991, Moscow, Vavilov str., 28

E-mail: MatseevichTA@mgsu.ru

Abstract. The compatibility of polymer structures was forecasted using the calculation scheme proposed by one of the authors for the analysis of polymer compatibility. The forecast was made for composite materials based on secondary polypropylene (PP) and short-chopped basalt fibers (BF). To verify the accuracy of the prediction, BF was treated with CCl₄ vapors in a flow reactor in order to replace oxygen atoms with chlorine atoms. Next, the chlorinated surface was treated in a stream of CH₄ to replace chlorine with hydrocarbon groups. Composites contained from 5 to 20% BF; each composite was heated at temperatures of 500, 650 and 750°C. The chemical structure of hydrocarbon groups most compatible with PP was determined by calculation using the Cascade computer program (INEOS RAS). IR studies, microanalysis, and X-ray fluorescence analysis showed the presence of such groups on the surface of BF that are chemically bonded to silicon atoms. The surface treatment performed by BF improves the mechanical properties of the composites. The modulus of elasticity reaches 2120 MPa with a BF content of 20% (for secondary PP this module is 705 MPa). The strength is 44,5 MPa (for secondary PP, the strength is 26,5 MPa). The specific impact strength reaches 18,3 kJ/m² (for the initial secondary PP, this value is 14,4 kJ/m²).

1. Introduction
In this work, we solved the problem of predicting the compatibility of hydrocarbon groups grafted onto the surface of BF with secondary PP. The presence of groups −H, ≡CH, =CH₂, −CH₃ improves compatibility of the fiber surface with PP and improves adhesion. In turn, this helps to improve the mechanical properties of the resulting composites.

Basalt fibers (BF) are currently very popular and are used to create polymer composites. In addition to good mechanical properties, basalt has high chemo and heat resistance [1-3], good thermal, electrical and sound insulation properties [4]. Polymer concretes based on a polybutadiene matrix with quartz sand and ash as reinforced components possess very high resistance to acids and alkalis,
excellent hardness and adhesion to metal elements introduced into the composite. Basalt can be used in a wide temperature range from -260 °C to 650 °C in comparison with fiberglass (from -60 to 450 °C) [4-6]. Replacing fiberglass with basalt fiber can reduce the risk of environmental pollution by highly toxic metals and their oxides, which are produced in the production of fiberglass. In addition, basalt fiber has a higher stiffness and strength than fiberglass. Therefore, basalt fibers are increasingly used and studied in composites based on a number of polymers [7-8].

As for PP, it has been widely studied in a number of works. We note the works [9-12], in which a complex of studies of relaxation properties of materials based on this polymer was carried out. Experiments were performed on stress relaxation under conditions of tension and compression at different temperatures and strains, master relaxation curves were obtained, and the regions of linear and nonlinear mechanical behavior were determined. The data obtained in [9-12] formed the basis of the monograph [13].

In practice, reinforced composites based on secondary PP in this work were prepared using short-chopped BF as filler. The surface of the BF was treated with CCl₄ vapor in a flow reactor in order to replace oxygen atoms with chlorine atoms. Next, the chlorinated surface was treated in a stream of CH₄ to replace chlorine with hydrocarbon groups. Such processing leads to the formation on the surface of BF, the chemical groups –H, =CH₂, =CH₂, –CH₂. The processing principle can be illustrated by the example of obtaining monodisperse carbon particles [14].

To analyze the structure and properties of composites in this work, we used the method of infrared (IR) spectroscopy with Fourier transform (IR-Fourier) in transmission mode. IR spectra were recorded using a Nicolet 360 FTIR spectrophotometer in the wave number range 400 - 4000 cm⁻¹. Also used the method of x-ray fluorescence analysis (XRF) using an energy dispersive spectrometer SSD X-Max (Oxford Instruments, UK). When studying mechanical properties, an IR-5046 tensile testing machine was used to obtain stress-strain curves at elongation and compression. When testing for bending and impact strength, the Dinstat device was used in accordance with DIN 53435. The tests were carried out for samples with a size of 15×10×4 mm without a notch.

Consider the model principles of polymer compatibility analysis. To assess the compatibility of PP with polymer structures, which are listed in Table 1, we used the model and calculation scheme proposed in [15-18]. Let us introduce the notation

$$\Phi = \frac{4(V_{p,1} \cdot V_{p,2})^{1/3}}{(V_{p,1}^{1/3} + V_{p,2}^{1/3})^{2/3}} \tag{1}$$

where $V_{p,1}$ and $V_{p,2}$ are the molar volumes of polymers 1 and 2, respectively.

Various situations are possible here:

1) With the introduction of the first polymer into the second:

$$\mu_1 = \frac{\delta_{p,1}^2}{\delta_{p,2}^2} > 1.374 \Phi \left( \Phi - \sqrt{(\Phi^2 + \frac{\gamma_{p,1}}{\gamma_{p,2}} - 2\Phi \left( \frac{\gamma_{p,1}}{\gamma_{p,2}} \right)^{0.5}} \right)^2 \tag{2}$$

When introducing a second polymer into the first:

$$\mu_2 = \frac{\delta_{p,2}^2}{\delta_{p,1}^2} > 1.374 \Phi \left( \Phi - \sqrt{(\Phi^2 + \frac{\gamma_{p,2}}{\gamma_{p,1}} - 2\Phi \left( \frac{\gamma_{p,2}}{\gamma_{p,1}} \right)^{0.5}} \right) \tag{3}$$

Here $\delta_{p,1}$ and $\delta_{p,2}$ are the solubility parameters of polymers 1 and 2, respectively; $\gamma_{p,1}$ and $\gamma_{p,2}$ are the surface energies of polymers 1 and 2, respectively. These inequalities describe a situation in which polymers are incompatible.

2) When small amounts of the first polymer are introduced into the second, the following inequality holds:
\[ \mu_1 = \frac{\delta_{p,1}^2}{\delta_{p,2}^2} < 1.374\Phi \left( \Phi - \sqrt{\Phi^2 + \frac{\gamma_{p,1}}{\gamma_{p,2}} - 2\Phi \left( \frac{\gamma_{p,1}}{\gamma_{p,2}} \right)^{0.5}} \right) \]  

(4)

those polymers are compatible.

However, when the second polymer is introduced into the first, it may turn out that the left side of the criterion is larger than the right, i.e. compatibility not observed.

\[ \mu_2 = \frac{\delta_{p,2}^2}{\delta_{p,1}^2} > 1.374\Phi \left( \Phi - \sqrt{\Phi^2 + \frac{\gamma_{p,2}}{\gamma_{p,1}} - 2\Phi \left( \frac{\gamma_{p,2}}{\gamma_{p,1}} \right)^{0.5}} \right) \]

(5)

3) When introducing the first polymer into the second and when introducing the second polymer into the first, the inequalities take place

\[ \mu_1 = \frac{\delta_{p,1}^2}{\delta_{p,2}^2} < 1.374\Phi \left( \Phi - \sqrt{\Phi^2 + \frac{\gamma_{p,1}}{\gamma_{p,2}} - 2\Phi \left( \frac{\gamma_{p,1}}{\gamma_{p,2}} \right)^{0.5}} \right), \]  

(6)

\[ \mu_2 = \frac{\delta_{p,2}^2}{\delta_{p,1}^2} < 1.374\Phi \left( \Phi - \sqrt{\Phi^2 + \frac{\gamma_{p,2}}{\gamma_{p,1}} - 2\Phi \left( \frac{\gamma_{p,2}}{\gamma_{p,1}} \right)^{0.5}} \right) \]  

(7)

This situation characterizes the full compatibility of the polymers.

Basalt fibers contain the largest amount of SiO₂ (~49%). First, we analyze the compatibility of SiO₂ and PP. We will carry out calculations using the Cascade computer program (INEOS RAS). For SiO₂, \( \delta = 13.9 \text{ (J/cm}^3\text{)}^{0.5}; \gamma = 21.6 \text{ mN/m}^2; V_m = 29.8 \text{ Å}^3. \) For PP, \( \delta = 16.2 \text{ (J/cm}^3\text{)}^{0.5}; \gamma = 36.1 \text{ mN/m}^2; V_m = 46.6 \text{ Å}^3. \) With the introduction of the first polymer into the second, as well as with the introduction of the second polymer into the first, relations (2) and (3) apply. Therefore, these polymers are not compatible.

The analysis showed that the best compatibility of PP with polymer structures on the surface of the BF is observed for the following structures (table 1):

**Table 1. Structures, their properties and compatibility with PP**

| №  | Structure          | Solubility parameter, (J/cm³)⁰.⁵ | Surface tension, mN/m² | Molar volume, Å³ | PP is introduced into this structure | This structure is introduced in PP |
|----|--------------------|----------------------------------|------------------------|------------------|-------------------------------------|----------------------------------|
| 1  | \[\text{CH}_3\]     | 16.2                             | 36.1                   | 46.6             | +                                   | +                                |
| 2  | \[\text{CH}_3\]     | 14.5                             | 20.4                   | 75.7             | +                                   | -                                |
| 3  | \[\text{Si–CH}_2\]  | 15.2                             | 21.9                   | 84.9             | +                                   | +                                |
The most favorable compatibility is observed for structure No. 3. This structure is fully compatible with PP. Structures No. 2, 4, and 5 are partially compatible with PP, since when evaluating their compatibility they obey relations (4) and (5). Thus, it is possible to improve the adhesion of PP to the surface of BF due to the compatibility of hydrocarbon groups grafted onto their surface. To prove the formation of hydrocarbon structures on the surface of BF, an XRF was performed. The results are shown in Figure 1.

![XRF spectra](image)

**Figure 1.** The results of the XRF of basalt fibers: \(a\) is the unmodified BF; \(b\) is the modified fiber at 500°C; \(c\) is the modified fiber at 650°C; \(d\) is the modified fiber at 750°C.

An analysis of the spectra (Figs. 1b - 1d) confirms the presence of hydrocarbon groups remaining after treatment of the surface of the explosives. It is also shown that the carbon content on the surface of modified BF is inversely proportional to the heat treatment temperature. Thus, the carbon content
on the surface of the sample with a heat treatment temperature of 750°C is much less than on the surface of the sample with a heat treatment temperature of 500°C. This observation can be explained by the fact that at sufficiently high temperatures, thermal degradation of hydrocarbon groups on the surface of the explosives is possible.

2. Experimental part
First of all, it is necessary to characterize the properties of the secondary PP used in this work. The melt flow rate of the secondary PP is 3.2 g/10 min. The density of the sample pressed secondary PP is 0.91 g/cm³. The crystallinity degree α was calculated by the usual formula and it was found that α = 62%. By the way, for the primary PP, the degree of crystallinity is α = 60%.

The thermomechanical curve of the secondary PP used in this work is shown in Figure 2.

![Thermomechanical curve of the secondary PP.](image)

Consider the mechanical properties of composites filled with modified basalt fibers. **Modulus of elasticity, bending strength, specific impact strength.** Each test was carried out from 4 to 6 times. The tensile test results of the samples are shown in table 2

| Processing temperature, °C | Share of BF, % | Modulus of elasticity, MPa | Strength, MPa | Strain at rapture, % |
|----------------------------|----------------|---------------------------|--------------|---------------------|
| 0                          | 705            | 26.5                      | -            |
| 5                          | 1060           | 33.1                      | 11           |
| 20                         | 1390           | 33.5                      | 10           |
| 15                         | 1860           | 34.2                      | 10           |
| 20                         | 1670           | 37.7                      | 9            |
| 5                          | 870            | 31.9                      | 13           |
| 10                         | 1330           | 33.6                      | 11           |
| 15                         | 1730           | 35.7                      | 9            |
| 20                         | 2120           | 37.9                      | 8            |
| 500                        | 1010           | 34.8                      | 20           |
| 650                        |                |                           |              |
From the above data it is seen that the introduction of short-chopped BF (5-20% wt.) in the composition of the polypropylene matrix causes an increase in the elastic modulus by a factor of 2-3: from 705 MPa to 1580-2120 MPa. Compared to unfilled secondary PP, the tensile strength of the obtained composites increased from 26.5 MPa to 38.0 MPa.

The bending strength and specific impact strength of the composites are given in table 3.

| Processing temperature, °C | Share of BF, % | Bending strength, MPa | Specific impact strength, kg·cm/cm² |
|---------------------------|----------------|-----------------------|----------------------------------|
| 650                       | 0              | 77.0                  | 14.4                             |
|                           | 5              | 63.0                  | 17.0                             |
|                           | 10             | 67.0                  | 18.3                             |
|                           | 15             | 74.0                  | 15.4                             |
|                           | 20             | 66.0                  | 13.6                             |
| 5                         | 69.0           | 16.5                  |                                   |
| 10                        | 71.0           | 18.0                  |                                   |
| 15                        | 73.0           | 14.7                  |                                   |
| 20                        | 72.0           | 14.3                  |                                   |
| 5                         | 72.0           | 11.1                  |                                   |
| 10                        | 73.0           | 14.6                  |                                   |
| 15                        | 70.0           | 10.0                  |                                   |
| 20                        | 65.0           | 5.3                   |                                   |
| 5                         | 76.0           | 13.4                  |                                   |
| 10                        | 73.0           | 11.4                  |                                   |
| 15                        | 66.0           | 7.1                   |                                   |
| 20                        | 66.0           | 8.0                   |                                   |

At moderate treatment temperatures, the specific impact strength increases. However, at the highest processing temperature (750°C), the specific impact strength becomes less than for unfilled PP. This is due to thermal oxidative degradation of hydrocarbon groups.

3. Conclusion
A model analysis of the prediction of the compatibility of hydrocarbon groups grafted onto the surface of BFs was carried out. For mathematical analysis, the Cascade computer program developed at INEOS RAS was used. To confirm the forecast, we performed a comprehensive study of the surface composition of BF as well as studied the properties of polymer composite materials based on secondary PP. The degree of filling of the composites ranged from 5 to 20% wt. An original method
for modifying BF in methane medium at fiber heat treatment temperatures of 500, 650, and 750°C was used. It was found that hydrocarbon groups are formed on the surface of BF, which is predicted by the forecast. This helps to improve the compatibility of the surface of BF with PP. It was found that the introduction of modified BF increases the elastic modulus of the composite by a factor of ~ 3 compared with an unfilled secondary PP. Specific impact strength and tensile strength also increase. All this contributes to the application of the obtained composites in the construction industry.

Acknowledgments

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References

[1] Subramanian R V, Tang T J Y and Austin H F 1977 SAMPE Quarterly pp 1-10
[2] Artemenko S E 2003 Fiber Chemistry vol 35 №3 p 226
[3] Sim J and Park C 2005 Composites Part B vol 36 № 6 p 504
[4] Van de Velde K, Kiekens P and Van Langenhove L 2003 Proceedings of 10th international conference on composites/nano engineering, University of New Orleans p 20
[5] Figovsky O, Beilin D, Blank N, Potapov J and Chernyshev V 1998 Cement and Concrete Composites vol 18 №6 p 437
[6] Sergeev V P, Chuvashov Yu N, Galushchak O V and Pervak I G 1994 Power Metallurgy and Metal Ceramics vol 33 №9-10 p 555
[7] Fire Resistant Board Material 2001: European Patent
[8] Zihlif A M and Ragosta G 2003 Journal of Thermoplastic Composite Materials vol 16 №3 p 273
[9] Askadskii A A, Pakhneva O V and Popova M N 2007 Plasticheskie massy №7 p 47
[10] Askadskii A A, Pakhneva O V and Popova M N 2007 Plasticheskie massy №8 p 45
[11] Askadskii A A, Golovanov A V, Pakhneva O V and Popova M N 2009 Vysokomol. Soedin, vol 51 №5 p 838
[12] Popova M N, Askadskii A A, Golovanov A V and etc 2009 Plasticheskie massy №6 p 40
[13] Askadskii A A, Matseevich T A and Popova M N 2017 ASV p 490
[14] Aleskovsky V B and Galitseiskii K B RF patent 2287543 Claim 05/23/2005 Publ 11/20/2006 Bull №32
[15] Askadskii A A 2003 Cambridge International Science Publishing p 696
[16] Askadskii A A and Khokhlov A R 2009 Nauchnyi Mir p 380
[17] Askadskii A A and Kondrashchenko V I 1999 Nauchnyi Mir vol 1 p 543
[18] Askadskii A A, Matseevich T A, Popova M N and Kondrashchenko V I 2015 Polymer Science, Series A vol 57(2) p 186