CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 5, No. 1, 2011 Chemical Technology

Denys Chervakov, Petro Bashtanyk and Mihail Burmistr

CONSTRUCTIONAL MATERIALS BASED ON CROSS-LINKED POLYPROPYLENE REINFORCED BY MODIFIED BASALT FIBERS

State Higher Educational Establishment "Ukrainian State University of Chemical Technology",
8 Gagarina Ave., 49005 Dnipropetrovs'k, Ukraine

Received: March 03, 2010 / Revised: May 25, 2010 / Accepted: September 30, 2010

Abstract. Technology of polymer materials production based on polypropylene reinforced by modified basalt fibers has been obtained. The experimental results of polypropylene modification by benzoyl peroxides and mixture of benzoyl peroxide with methylvinylcyclosiloxane on mechanical properties of composite material have been shown. It has been established that composite materials based on crosslinked polypropylene reinforced by basalt fibers which are dressed by polyepichlorohydrin resins have the increased mechanical and thermo-physical properties.

Keywords: crosslinked polypropylene, benzoyl peroxide, methylvinylcyclosiloxane, modification, dressing agents, basalt fibers.

1. Introduction

State-of-the-art of industrial development requires a continuous state of polymer materials exploration, the properties of which could change on demands for finished products (high strength, hardness, thermal conductivity, *etc*.). That way allows to obtain three-dimensional structure due to intermolecular chemical bonds formation that leads to service properties increase [1].

Nowadays the industry uses the next ways of polyolefins crosslinking: by radiation treatment and by chemical crosslinking (by introduction of chemical reactive compounds, such as peroxide and silane, into polyolefin).

Polyolefin crosslinking by silane is one of the most effective ways to improve its thermal and chemical stability, physico-mechanical properties, barrier properties, and to produce products with improved configuration [2]. Production of such crosslinked polymer composition materials can proceed *via* combining a polymer melt with peroxide and silane oligomers. Processing into goods with simultaneous crosslinking can take place using standard equipment for plastic processing.

A new method of polymer composite materials production (PCM) based on polyolefin thermoplastic matrix, in particular based on crosslinked polypropylene (CPP) and mineral reinforcing filler was proposed by us at first.

2. Experimental

2.1. Materials

During the researches basalt fiber ZHBTR-0-330 (TU 00292729.001-96) was used as a filler. Diameter of elemental fibers was 12.9 ± 1.7 mcm, tensile strength – 1433 ± 417 MPa, relative elongation at break – 2.26 ± 0.75 %. Polypropylene A4-71K (TU U 54008400.001-97) was used as a polymer matrix.

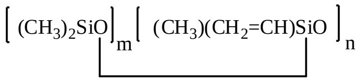
2.2. Methods of Composite Materials Production

Combining the basalt fibers with polypropylene was carried out in a screw-disk extruder in the normal stresses zone at temperature of 483 K. Production of standard samples was done on the injection molding machine Kuasy 25x32/1 (Germany) at following temperatures by zones: 1 – 433 K, 2 – 463 K, 3 – 483 K. Mechanical and thermo-physical properties of composites were determined according to the standards for plastics.

2.3. Polypropylene Modification

Polypropylene (PP) structure modification was carried out by dressing a benzoyl peroxide solution in acetone and polysiloxane polyol solution in *iso*-propanolic alcohol on its surface.

Structural formula of methylvinylcyclosiloxane is shown below:



$$\left[(CH_3)_2SiO\right]_m\left[(CH_3)(CH_2{=}CH)SiO\right]_n \qquad (1)$$

where $m+n = 3–5$, $m = 1–5$, $n = 5–1$

After a step which was shown earlier the obtained mixture of components was processed on the screw-disk extruder in the normal stresses zone at temperatures of 483 K.

2.4. Basalt Fibers Activation

Estimation of basalt fibers (BF) usage activated by acid or alkali treatment [3, 4] was conducted. It was established, that the basalt fiber treated by alkali has a lower value of tensile strength than that of the initial one and basalt fibers treated by acid.

Properties of basalt plastics based on polypropylene reinforced by basalt fibers, which were activated by 0.1 N and 1 N NaOH solutions were studied. During the research of influence of treatment time of basalt fibers by 0.1 N NaOH solutions on basalt plastics properties, we obtained composite materials with higher values of tensile strength and impact elasticity. This increase is not considerable, that is why we carried out research of basalt fibers treatment by 1 N solution of NaOH. It was determined that after the treatment of basalt fibers by 1 N solution of NaOH a slight decrease of composite tensile strength occurs. However, the composite impact strength increases from 19.7 KJ/m^2 (initial BF) to 26.1 KJ/m^2 (after 60 min of treatment). Therefore, we got a composite material with the impact strength that is significantly higher than that in the basalt plastic reinforced by the initial basalt fiber [3]. It should be mentioned that fibers activated in such a way have been used by us for reinforcement of composite materials for a long time [3-5]. Functional groups that are formed on BF surface are able to interact with dressing agents of different nature on principle. Therefore, activated fibers can be used for polyolefins reinforcement.

Thus, BF activation leads to significant changes in a filaments surface structure. It has been found that higher chemisorptions interactions were observed between polypropylene matrix and basalt fibers, treated by the alkali. That is a consequence of formation of functional groups [4] on the basalt fiber surface, which in essence are able to interact with various dressing agents.

2.4.1. Basalt fibers dressing

For the purpose of basalt fibers surface modification we used polyepichlorohdrin rubbers HYDRIN (USA) type as dressing agents [3]. The main feature of selected dressing agents is the presence of electron-donor oxygen atoms (–O–) of ether bonds, reactive (Cl–CH_2–) chloromethyl groups and (CH_2=CH–) unsaturated fragment (only for Hydrin T3000) in their structure, which are able of chemosorptional interaction with active functional groups of the filler, as well as with structural fragments (functional groups) to some extent.

3. Results and Discussion

Modifications of polypropylene by benzoyl peroxide (BP) and a mixture of benzoyl peroxide and methylvinylcyclosiloxane (MVCS) that acts as crosslinking additive on account of vinyl groups were carried out. It is expected that such approach allows to create PCM with crosslinked polypropylene matrix during its processing. We conducted comparative analysis of physico-mechanical properties of crosslinked polypropylene matrix and PCM on its basis that is reinforced by BF. Polypropylene properties depended upon benzoyl peroxide are shown in Table 1.

Table 1

Properties of polypropylene depending on the benzoyl peroxide content

Properties	Benzoyl peroxide content, wt %				
	0	0.25	0.50	0.75	1.00
Melt flow index, g/10 min	2.29	2.80	3.91	5.50	2.87
Density, kg/m^3	902	860	858	857	860
Tensile strength, MPa	26.0	31.3	31.5	31.4	32.4
Relative elongation, %	109	162	135	38	29
Impact elasticity by Sharp, KJ/m^2	70.7	74.7*	41.7*	40.9*	21.0*
Shrinkage, %	1.37	1.17	1.17	0.8	0.75
Thermal stability by Vicat, K	413	414	414	415	410

Note: *– fragile destruction

It should be noted that the properties of modified polypropylene depend on the content of benzoyl peroxide in its composition. It was established that for polypropylene containing 0.25 % of BP, tensile strength values grow by 16 % and the slight increase of impact elasticity by Sharp (from 70.7 to 74.7 KJ/m^2) is observed. It should be noted that for all modified polypropylene samples the fragile destruction is established.

At a higher BP content in the polymer matrix (0.5–1.0 %) one can observe: color changing for testing samples from white to light yellow, significant reduction of relative elongation of testing samples at break. It can be the result of destruction processes and polymer matrix crosslinking. In order to determine the temperature range of peroxide crosslinked polypropylene workability, we used a thermogravimetric (TG) and DSC analyses.

Samples analyses by TG method of initial and modified polypropylene are shown in Fig. 1.

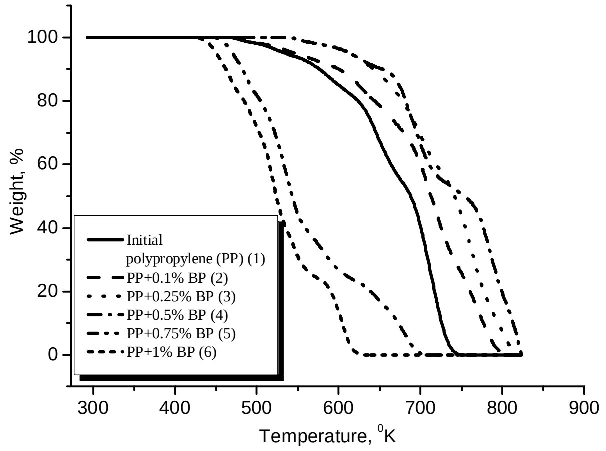


Fig. 1. Results of thermo-gravimetric analysis of the initial (1) and the modified polypropylene (2-6) depending on concentration of BP (%): 0.1 (2), 0.25 (3), 0.5 (4), 0.75 (5) and 1 (6)

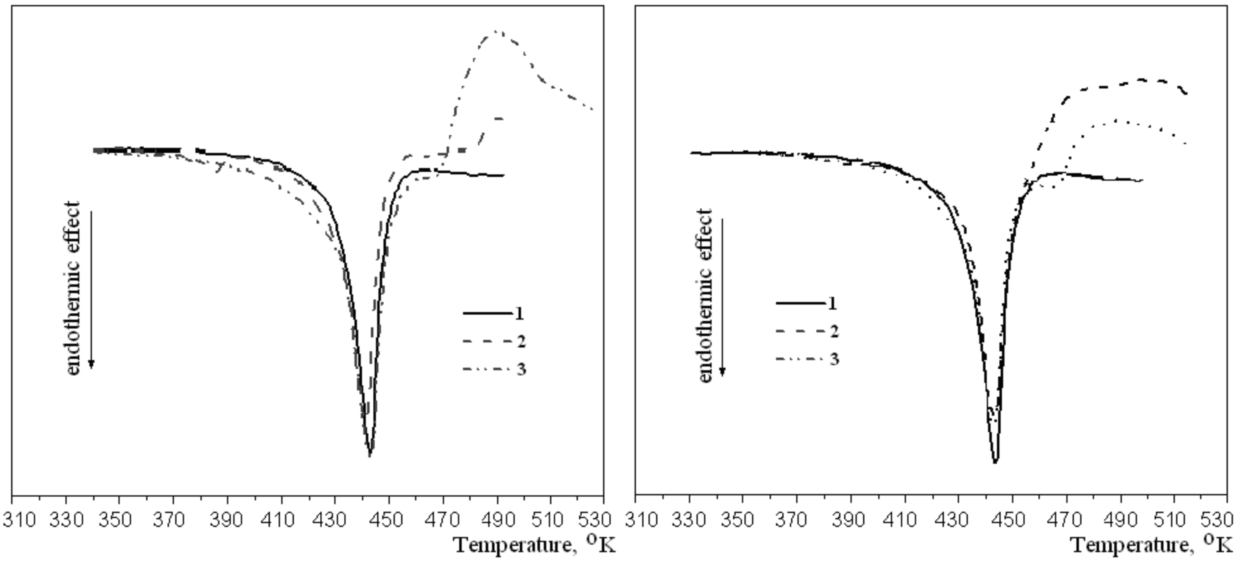
The obtained results show that the adding of 0.1–0.5 % of BP in polypropylene polymer matrix provides significant improvement of its thermal stability: from 591 to 680 K (at samples weight loss of 10 %). At the same time we can observe a decrease of CPP thermal stability at peroxide content from 0.5 to 1.0 %. May be it is the result of the larger number of unstable macroradicals formation that destruct with polymer chain breaking (β-destruction) [1]. Improvement of polypropylene stability at the content of 0.1–0.5 % of BP can be explained by thermostable –C–C– links formation between PP macromolecules during peroxide crosslinking.

DSC data analyses of initial and modified polypropylene are shown in Fig. 2.

For all studied samples the intensity of PP melting peak decrease occurs at 446 K which can be the result of polypropylene structure amorphization.

However, at the same time, for crosslinked PP containing 0.1–0.5 % of BP within the temperature range of 458–478 K the appearance of additional structure entities capable for the melting process is observed.

The current results are probably a consequence of polypropylene supramolecular structure changes (formation of new structures, possibly due to elimination of polypropylene unsaturated end-groups, as well as the appearance of transverse carbon-carbon linkages between polymer chains). To determine the nature of these changes it was necessary to investigate the detailed morphology of crosslinked PP by X-ray diffraction methods of analysis, which was not the purpose of these studies. Expansion of melting temperature of crosslinked PP allows to explain its increased melt flow index (Table 1). Disappearance of a second melting peak (in crosslinked PP containing 0.75–1 % of BP) at 452–473 K for crosslinked PP and the appearance of exothermic effects is the result of PP destruction beginning.



a) b)

Fig. 2. Results of DSC analysis of the initial (1a, 1b) and modified polypropylene (2-3) depending on concentrations of BP (%): 0.10 (2a), 0.25 (3a), 0.50 (2b) and 0.75 (3b)

Table 2

Properties of crosslinked polypropylene depending on the content of the methylvinylcyclosiloxane (content of benzoyl peroxide – 0.25 wt %)

Properties	Methylvinylcyclosiloxane, wt %					
	0	0.10	0.20	0.25	0.50	0.75
Melt flow index, g/10 min	2.8	4.1	5.0	5.5	5.5	4.7
Density, kg/m^3	860	889	867	855	841	838
Tensile strength, MPa	31.3	29.7	30.0	30.3	30.1	30.3
Relative elongation, %	162	40	41	42	48	55
Impact elasticity by Sharp, KJ/m^2	74.7	32*	36*	47*	52*	53.1*
Shrinkage, %	1.17	1.37	1.17	1.17	1.17	1.26
Thermal stability by Vicat, K	415	424	425	426	426	426

Note: *– fragile destruction

Table 3

Mechanical properties of basalt plastics based on crosslinked matrix depending on dressing and activation of basalt fibers (degree of filling is 20 wt %)

Type of modification	Properties						
	Melt flow index, g/10 min.	Density, kg/m^3	Tensile strength, MPa	Relative elongation, %	Impact elasticity by Sharp, KJ/m^2	Shrinkage, %	Thermal stability by Vicat, K
Polypropylene + initial basalt fiber	1.90	1009	30.1	34.0	20.4	1.17	418
Polypropylene + basalt fibers (activated by 1 N NaOH 40 min.)	1.60	1029	33.1	19.0	26.1	1.13	421
PP-BP- MVCS + basalt fibers (activated by 1 N NaOH 40 min.)	1.30	935	36.4	14.0	20.8	0.71	434
Polypropylene + basalt fibers (activated by 1 N NaOH 40 min)+ 1 % of HYDRIN H75 [5] on 100 g of BF	2.38	1023	36.5	30.0	24.5	0.80	442
PP-BP- MVCS + basalt fiber (activated by 1 N NaOH 40 min) + 1 % of HYDRIN H75 on 100 g of BF	1.24	965	41.9	13.4	21.4	0.83	442
Polypropylene + basalt fiber (activated by 1 N NaOH 40 min)+ 1 % of HYDRIN T3000 on 100 g of BF [5]	2.38	1022	35.0	22.0	26.7	0.90	441
PP-BP- MVCS + basalt fiber (activated by 1 N NaOH 40 min) + 1 % of HYDRIN T3000 on 100 g of BF	1.92	967	34.2	10.5	38.4	0.91	440

On the basis of obtained results, for further studies the optimum content of benzoyl peroxide – 0.25 wt % was chosen. At this concentration of PB the increase of heat resistance of modified polypropylene from 591 to 680 K (for weight loss of 10 %) and the slight improvement of its mechanical properties (impact elasticity and tensile strength) are observed. However, in our opinion, the usage of BP in the amount of 0.25 wt % will allow to realize the interaction between modified polypropylene and crosslinking agent – methylvinylcyclosiloxane – at most.

Using of methylvinylcyclosiloxane will provide a higher level of adhesion contact in the "polymer-fiber" system. Vinyl groups of this additive will provide the interaction with the polypropylene polymer matrix at the expense of copolymerization by double bonds. At the same time silica fragments probably provide the interaction with the mineral filler – basalt fiber.

Properties of CPP, modified by the mixture of BP and methylvinylcyclosiloxane are shown in Table 2.

The obtained results have shown that adding of a methylvinylcyclosiloxane to the composition for a crosslinked PP obtaining increases rates of links without the increase of BP concentrations. Functional groups of methylvinylcyclosiloxane that may graft on polypropylene are possibly interact with the surface of mineral fillers.

According to the obtained results 0.25 wt % of BP and 0.75 wt % of MVCS we took as an optimum content in polymer matrix.

Mechanical properties of obtained basalt plastics based on crosslinked matrix modified by initial, activated and dressed basalt fibers are shown in Table 3.

In the case of basalt fibers use modified by 1 wt % of HYDRIN H75 as the reinforcing filler and the use of PP-BP-MVCS as the polymer matrix allow to increase the composites tensile strength by 14.7 %. The improvement of physico-mechanical and thermo-physical properties while using activated basalt fibers dressed by HYDRIN T 3000 dressing agents (impact elasticity increase by 9.7 %) is noted.

Increasing of mechanical and thermo-physical properties of construction materials can be the consequence of the reinforcing filler surface state and interactions of functional groups, which appeared as a result of the MVCS and BP mixture introduction with the surface of modified basalt fibers into the polypropylene.

4. Conclusions

Such way of polypropylene modification allows to adjust the physico-mechanical properties of composite materials without using additional equipment. Developed materials can be used for the creation of such modern highways as geonets.

References

[1] Panzer L. and Bizang V.: Plasticheskie Massy, 1998, **3**, 3.
[2] Lien K. and Reid W.: Pat. WO 9221721, Publ. Dec. 10, 1992.
[3] Chervakov D., Bashtanyk P. and Burmistr M.: Voprosy Khimii i Khim. Tekhn., 2009, **3**, 100.
[4] Chervakov D., Bashtanyk P., Burmistr M. *et al.*: Voprosy Khimii i Khim. Tekhn., 2006, **5**, 166.
[5] Chervakov D., Bashtanyk P. and Burmistr M.: Voprosy Khimii i Khim. Tekhn., 2007, **4**, 98.
[6] Chervakov D., Bashtanyk P., Burmistr M. *et al.*: Voprosy Khimii i Khim. Tekhn., 2008, **6**, 77.

КОНСТРУКЦІЙНІ МАТЕРІАЛИ НА ОСНОВІ ЗШИТОГО ПОЛІПРОПІЛЕНУ, АРМОВАНОГО МОДИФІКОВАНИМИ БАЗАЛЬТОВИМИ ВОЛОКНАМИ

Анотація. *Розроблено технологію отримання полімерних композиційних матеріалів на основі поліпропілену, армованого модифікованим базальтовим волокном. Наведено результати експериментальних досліджень впливу модифікації поліпропілену пероксидом бензоїлу та суміші пероксиду бензоїлу з метилвінілциклосиланом на механічні властивості композиційного матеріалу. Встановлено, що така модифікація приводить до покращання механічних та теплофізичних властивостей композиційних матеріалів на основі зшитого поліпропілену, армованого базальтовими волокнами, поверхня яких апретована поліепіхлоргідриновими смолами.*

Ключові слова: *поліпропілен, зшитий поліпропілен, пероксид бензоїлу, метилвінілциклосилан, модифікація, апрети, базальтове волокно.*