

Reinforcement of Polymers by Means of Modification with an Implementation of Porous Fillers

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doi: <http://dx.doi.org/10.13005/bbra/1566>

(Received: 30 October 2014; accepted: 05 December 2014)

The presented paper demonstrates effectiveness of an application of fillers in polymer on an example of plasticized polyvinylchloride composites and carbamide foamed plastics with expanded perlite sand. The studies of structure and properties of optimal compositions of developed materials are presented.

Key words: Reinforcement, Polymers, Porous fillers.

Currently, the term “perlite” is defined as a natural glassy rock, with an ability to swell in a case of fast heating, resulting in a very porous pumice-like product. Use of perlite allows to produce from standard raw materials a material with specified properties: weight, strength and structure.

Expanded perlite sand (EPS) is used in cryogenic equipment as a thermal filler, which is after that is stored at disposal sites. It is established, that previously used EPS doesn't show a decrease in thermal insulation properties, which can be taken into account in a case of its application as effective filler of polymers. In particular, that applies to PVC linoleum with thermal insulation basis, where one of the most important characteristics (especially for the consumer products) is heat saving, and foamed plastics,

which are traditionally used as effective insulating materials. Therefore, in the presented study, on a basis of analysis of EPS properties, EPS prospectiveness as filler for plasticized PVC and carbamide composites is demonstrated.

EPS consists of, generally, from porous colorless transparent aluminosilicate glass and has a type of structure with open pores. Pores inside grains of EPS are of spherical or slit-like shape, their sizes vary from 0.5 to 10 μm [1]. Volume of open pores is, approximately, 75%.

Before using, EPS was separate into 4 factions, with the following sizes, mm: more than 0.25, 0.25-0.16, 0.16-0.063, less than 0.063. Bulk density data showed, that the highest bulk density was detected in a case of EPS with the smallest size of grains (less than 0.063 mm) due to denser packing of particles and EPS with particles larger than 0.25 mm, because particles that fraction contain dense areas of aluminosilicate glass without pores.

Particles of waste EPS are characterized by a large variation of parameters, therefore its

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separation into fractions was carried out; data on contents and bulk density is represented in table 1. Not separated EPS has the lowest density.

From table 1 it's clear, that large EPS particles with sizes more than 250 μm and the finest fraction with less than 60 μm size has the highest bulk density. Microscopy of EPS demonstrated, that particles with more than 250 μm size have dense glassy areas without pores, which explains higher bulk density. In a case of a fraction with less than 60 μm size, high bulk density is related with denser packing of particles.

Results of chemical analysis allow conclude, that EPS is a typical acidic aluminum silicate (table 2). Considering the chemical composition, the mineral composition was identified. EPS is 98% presented by amorphous in X-Ray volcanic glassy phase (Fig.1). Maximum diffraction profile is achieved at 3.76 $^{\circ}\text{A}$. There are traces of quartz (4.26-3.35-1.819) and potassium feldspar – 3.21 (KSi_3O_8).

EPS separation slightly changes the ratio of minerals. The data is presented in table 3. In the fine fraction there are no mica and amphibole, but pyroxene is reliably detected. X-Ray diffraction analysis allowed to calculate a proportion of amorphous phase, which varies depending on EPS fraction.

Thus, it is established that EPS can be characterized by a type of structure with open pores, which results in low bulk density (35 kg/m^3) and high adsorption of low-molecular liquids and gases by EPS. Low density EPS provides good thermophysical properties for polymer filled with EPS. High adsorption of EPS can facilitate EPS pores' filling by a melt of polymer (in a case of its application as filler in PVS composites, which are produced from melt) or a solution of polymer (in a case of an application as a component of binders for manufacturing of carbamide foamed plastics from carbamide-formaldehyde resins). It can be expected, that contact surface between polymer and filler will seriously increase, as a consequence, increased strength of polymer due to mechanical interlock will be obtained.

The results of modification of plasticized PVC composites:

It is established, that in a case of mixing with PVC-composites, absorption of plasticizer by pores of EPS takes place, therefore, problems at a

stage of mixing appear. We propose the method, which allows to use more porous filler (almost 100 mas.fr. for EPS for 100 mas.fr. of polymer): preliminary mixing of plasticizer with porous filler allows to obtain a virtually friable mixture, which combines well with other components mixture. In further temperature plastication in rolling equipment, a desorption of plasticizer, leading to reduced viscosity of melt, takes place, in consequence, workability is increased.

The study of processing and operational properties PVC-composites demonstrated, that:

- a) Thermal stability of PVC in a case of EPS introduction has a tendency for increase, the greatest effect is achieved in a case of a coarse filler. The reason for thermal stability increasing effect of EPS particles, probably, can be attributed to a porous structure of particles and high content of oxides of sodium and potassium and low content of iron oxides. A porous structure of particles of EPS determines a physical mechanism for a stabilization of polymer, due to sorption of hydrogen chloride and diminishing of its autocatalytic actions at polymer's destruction². A presence of iron oxides usually has a negative impact on thermal stability, therefore, their presence in a composition of EPS only in a very small quantities is a positive factor, which does not cause acceleration of destructive processes of polymer;
- b) Viscosity of melts is the greatest for composites with not separated EPS, in a case of an application of fine fractions even a decrease of a melt's fluidity factor had been detected, i.e. an increase of a melt's viscosity, which is, presumably, related with an absence of open porosity, therefore, there are the same patterns, which are characteristic for dispersed fillers with a comparatively large size of particles³⁻⁵.
- c) Mechanical properties of plasticized PVC-composites, in a case of filling with expanded perlite, in spite of the fact, that particles are porous and are of quite large size (as compared with the major part of traditionally used fine-dispersed mineral fillers), are reduced insignificantly. In cases of up to 10 mas.fr. of filler used, tensile strength remains

almost the same as compared with polymer without filler. That is a positive fact, because, in addition to a reduction in density of specimens, a decrease of heat conductivity coefficient due to filling of composites by light fillers, the developed materials have sufficiently high mechanical properties, water resistance, etc., which allows to recommend them for use in compositions of materials for floors' covering in exterior and middle layers, because EPS allows to obtain transparent colorless materials;

- d) water absorption increases with a concentration of EPS in compositions, its

largest values are in a case of an application of coarse particles, which is related to, the same as in a case of thermal stability, with a presence of open pores and water absorption.

Thus, although, according to some indicators, separation into fractions gives positive results, in a whole, considering material expenditures and sufficiently large manufacturing process-related problems in a case of EPS separation, more effective is use of not separated EPS, especially, taking into account, that in a process of processing in rolling equipment, mechanical grinding of large particles in polymer matrix takes place.

Table 1. Particle size distribution of EPS

No	Fraction, μm	Bulk density, kg/m^3	Fraction content, %
12345	< 60	39	10
	60-160	35	15
	160-250	32	20
	> 250	40	55
	Not separated	36	-

Table 2. Chemical composition of EPS.

% content relatively to weight of an absolutely dry sample													
SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MnO	MgO	Na_2O	K_2O	P_2O_5	SO_3	Cr_2O_3	Ignition loses
74.93	0.08	12.38	0.55	0.36	0.91	0.09	0.17	3.29	4.64	0.02	<0.05	-	2.22

Table 3. Mineral composition of various fractions of EPS

EPS fractions	Relative intensity / reverse interplanar space, nm minerals										Proportion of amorphous phase
	mica	quartz	feldspar	amphibole	pyroxene						
Not separated	0.32	0.8	1.00	0.55		0.46					
	1.008	2.35	2.99	3.135	-	3.37	-	-	-	-	0.98
> 250 μm	0.30	0.52	0.71	0.45	1.00	-	-	-	-	-	0.76
	1.008	2.351	2.984	3.128	3.18						
from 250 μm to 160 μm	0.29	0.61	0.71	0.5	-	1.00	0.45	-	-	-	0.84
	1.008	2.35	2.98	3.11		3.40	3.47				
from 160 μm to 60 μm	0.3	0.95	0.94	0.61	-	-	-	0.3	-	-	
	1.015	2.36	3.00	3.12				4.70			1.00
< 60 μm	-	0.46	-	1.00	-	0.38	0.32	0.26	0.34		0.63
		2.99		3.125		3.31	3.47	4.68	5.07		

Data, presented in tables 4 and 5 shows^{6,7}, that use of porous mineral filler as a component of a composition within 55-75 mas.fr. improves hardness, reduces residual deformation, abrasion resistance and density.

The results of modification of carbamide foamed plastic

Low density of EPS, which is close to density of carbamide foamed plastic, provides good thermalphysic properties of filled carbamide foamed plastic. High hygroscopicity of EPS facilitates filling of EPS pores by polymer, which leads to a big increase of contact surface between polymer and filler, as a consequence, strength of polymer due to mechanical interlock increases.

An increase of a proportion of amorphous phase, which mainly consists of SiO₂, increase an amount of isolated Si-OH groups on a surface. According to a mechanism of water adsorption in silicas¹, water molecules, adsorbed on those groups, interact with neighboring siloxane surface zones, forming two new silanol groups, which may inhibit a process of hardening of carbamide-formaldehyde oligomer in boundary layers due to formation of hydrogen links with functional groups of resin.

Therefore, it can be presumed, that it is preferable to use fraction with the highest proportion of amorphous part, i.e. fractions from 160 to 60 µm and not separated EPS.

Table 4. Compositions of PVC-composites (mass.fr.)

Components of a composite	Components content, mass.fr.		
	Composting No1	Composting No 2	Composting No 3
PVC	100	100	100
Dioctylphthalate	45	45	45
Calcium stearate	2	2	2
Expanded perlite sand	55	60	75

Table 5. Properties of PVC composites

Property	Value		
	No 1	No 2	No 3
Hardness, kg/mm ²	0.37	0.42	0.45
Abrasion resistance, µm	32	37	42
Density, kg/m ³	1470	1465	1435
Absolute residual deformation, mm	0.21	0.22	0.30

Table 6. Properties of carbamide foamed plastics

Property	Without filler	Carbamide foamed plastic, filled with EPS fraction < 60 µm (5 mass.fr.)	Carbamide foamed plastic, filled with EPS fraction 60-160 µm (5 mass.fr.)
Density, kg/m ³	20	38	36
Compressive strength at 10% linear deformation, MPa	0.007	0.040	0.038
Flexural strength, MPa	0.001	0.003	0.002
Elastic modulus, MPa	0.07	0.92	0.83
Sorption wetting at 24 hours, mass. %	20	11	12
Thermal conductivity coefficient, w/ (m · To)	0.034	0.035	0.036
Linear shrinkage, %	10	1.8	1.5

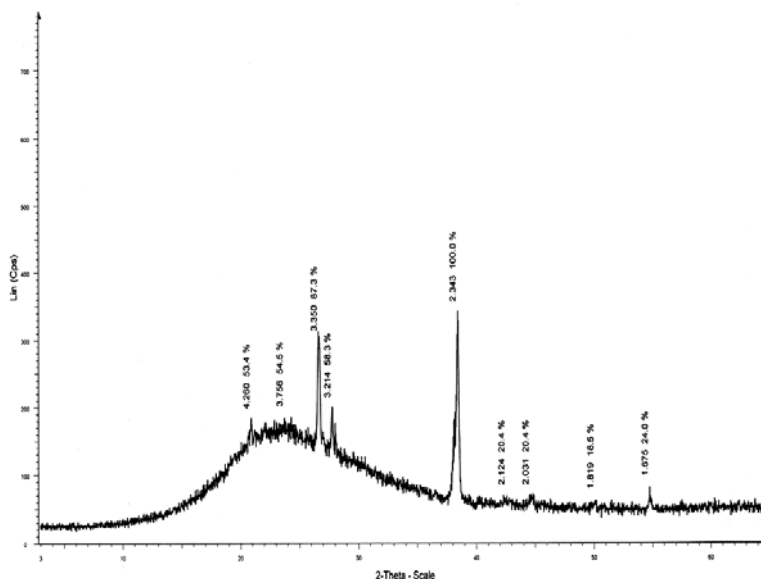


Fig. 1. Expanded perlite X-Ray diffraction spectrum

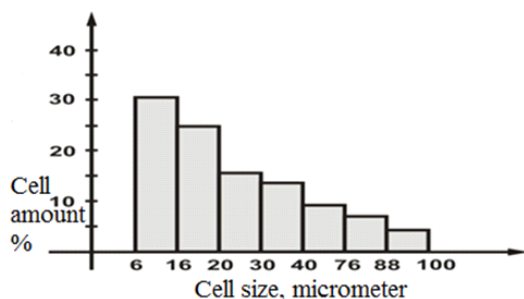
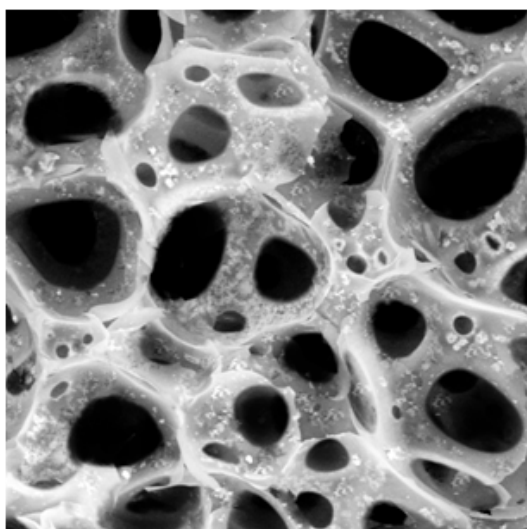


Fig. 2. Styrofoam microphotograph and cell size gistogram

Structure with open pores determines high hygroscopicity of EPS. At the same time, it is worth noting, that speed and amount of absorbed water is more than resin, and it is increasing with an increase of size of factions. Presumably, it is due to the fact, that large particles of EPS has high specific surface inside the particles, which facilitates immediate adsorption of larger amount of water.

The key feature of filling of foamed plastics is a redistribution of filler particles between elements of cellular structure, which can be viewed as a peculiar “autoselectivity” of foamed system to filler, depending on its dispersion. Volumetric fillers, to which coarse fractions of EPS can be attributed, can have a negative influence on a formation of cellular structures of foamed plastics due to an uneven distribution of large particles of EPS in elements of cellular structure.

The study of structures of foamed plastics with use of optical and electronic microscopy showed, that EPS of finner fractions are distributed in polymer matrix of foamed plastic more evenly (Fig.2), and it is filling both joints and rods of a cell structure, which leads to an increase of mechanical properties.

From analysis of the results of the study of structural, technological and operational data

[8-10], optimal compositions of carbamide foamed plastic were selected, which are using following fractions of EPS: less than 60 μm , from 60 to 160 μm . Table 6 presents values of main properties of carbamide foamed plastics, containing 5 mass.fr. of EPS, of the above-mentioned fractions, because with that concentration specific strength has the maximum value.

Compositions of carbamide foamed plastics, filled with EPS, that are listed in table 6, has a good combination of manufacturing and technical properties, in particular: increased compression strength (80% higher as compared to an analogous composite without filler), low sorption wetting (40-45% less) and low values shrinkage deformations (1.3 %), while maintaining high thermal insulation properties (thermal conductivity coefficient 0.035 W/(mK)).

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