

Modified Densified Waste of Expanded Polystyrene and Its Blends With Polyamide 6

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The regularities of expanded polystyrene (EPS) waste modified by polyvinylpyrrolidone (PVP) with the simultaneous gas release in various solvents were revealed. The upper sorption limit depends on the nature of the solvent, the concentration and molecular mass of the PVP, the temperature of the process, and the apparent density of the EPS. It was established that the sorption limit of PVP increases with increasing of its concentration in the system and decreases with molecular mass increasing. Based on XRD and FTIR analyses, it was determined that materials based on polyamide 6 and EPS modified by PVP have an increased crystallinity degree by 10–15%, a smaller average crystallite size and higher technological compatibility. The addition of PVP-modified EPS contributes to the increase of the yield strength of polyamide 6 by about 5%–10%. The increase of the Vicat softening point by 5–8 K and the surface hardness by 25–30 MPa of materials based on polyamide 6 and modified polystyrene was investigated. It is caused by the redistribution of intermolecular bonds between the components of the blend under by the effect of a uniformly distributed PVP in the EPS resulting in increased compatibility between the components and the compacted structure. POLYM. ENG. SCI., 00:000–000, 2020. © 2020 Society of Plastics Engineers

INTRODUCTION

The problem of recycling polymer materials is the matter of great interest. It is caused by their widespread use in a variety of industries, which, together with the lack of efficient and economical utilization methods, leads to their significant accumulation in household and industrial waste. Such accumulation in waste poses a serious environmental threat, which is increasingly being addressed by regulations and prohibitions [1]. In many cases, these regulations provide for the obligatory sorting of polymeric materials, which sufficiently simplifies the development of effective technologies for the recycling of polymers to obtain after-products, and enables to solve a number of acute social, economic, and environmental problems.

Polystyrene in the form of a foamed product is widely used for the production of packaging and heat-insulating materials. The positive properties of expanded polystyrene (EPS) at the same time are a significant obstacle to developing a technology for its disposal. The recycling of expanded thermoplastics by conventional methods such as injection molding and extrusion requires

an overcare due to the presence of gas inclusions [2], which during polymers melting adversely affect the uniformity of moldings and the quality of end products with relatively low productivity of equipment. In this regard, one of the main technological tasks is the development of methods for raw materials preparing that would minimize this negative impact. The simplest technologies of disposing of EPS involve its use as a filler for new materials, such as light concrete [3–7], or highly effective heat-insulating plaster mortars [8].

For reuse of EPS as a raw material deprived of gas phase the technology that uses the heat treatment method and allows to reduce the initial volume of EPS by 10–20 times is proposed [9]. However, the emissions of harmful substances at high temperatures are typical for this method [10].

The technologies of EPS utilization are suggested, which include the possibility of mixing of expanded waste with other materials. The process of obtaining a composite on the basis of natural rubber [11] or coconut shells [12] with EPS waste was investigated. The main problem, in this case, is the incompatibility of the mixture components. For its promotion the method of maleic anhydride grafting for obtaining of copolymers was used. This led to obtaining a composite with higher physico-mechanical properties.

However, among methods for expanded materials preparing for recycling, the most effective from an economic and technological point of view are methods based on the complete or partial removal of gas inclusions without pressure, namely by heating of plastic foam waste in air or in the liquid phase. There are methods [13–16] of EPS waste compaction with solvents that reduce the volume of a polymer. The most effective solvents are acetone, ethyl acetate, and tetrahydrofuran, which reduce the volume of PS in 2, 5, and 8 s, respectively. According to this method, EPS waste is grinded and sprayed with a sealing solvent containing an expanding agent (aliphatic or aromatic hydrocarbons, alcohols). The resulting polystyrene contains 5%–10% of the expanding agent.

At the same time, the creation of polymeric composite materials based on polymer blends by physical or chemical modification of high production volume thermoplastic and thermosetting polymers is the most rational way of obtaining of new materials with all necessary properties. In particular, methods for the polyvinyl chloride modification by polystyrene plastics and the unsaturated polyester resins modification by polyvinyl chloride have been developed [17–19]. There are also known materials based on blends of polyamide 6 with polystyrene [20], obtained by mixing in a viscous-flow and obtained with the use of compatibilizers and inorganic fillers [21, 22], or blends of polyamide 6 with ABS [23]. These materials have low technological shrinkage and water

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absorption and good performance properties. It is especially important for of constructional products. However, thermodynamic incompatibility of these polymers negatively affects the physical and mechanical properties of modified materials. As is known [24], the materials based on polymer mixtures have the optimum mechanical properties only when the components of the mixture are sufficiently compatible but do not form a homogeneous system due to the mutual dissolution. There are several methods to increase the compatibility between thermodynamically incompatible components [25], one of which is the previous physical or chemical modification by functionally active compounds.

At the same time the combination of stages of preparation of secondary raw materials for processing with modification of functional active macromolecular compounds provides the necessary specific properties for materials from EPS waste. Such approach gives a possibility to regulate technological and operational properties and significantly expand the scope of the materials.

For the modification of EPS waste, water, and alcohol soluble surfactant polymer—polyvinylpyrrolidone (PVP)—has been selected. It has a complex of unique properties in the polymer blends [26], namely selective permeability, sorption ability, regulated water sorption, and also high activity to the different surfaces [27]. It is known that polyamides with PVP are thermodynamically compatible and form colloidal solutions. It allows predicting and increasing of compatibility between components of a mixture based on polyamide and modified polystyrene.

Thus, the development of modification technology of EPS wastes and the creation of molding materials of structural designation based on the polystyrene modifier and polyamide 6 is a crucial scientific and technical task in the field of polymeric and composite materials technology.

MATERIALS AND METHODS

High-purified PVP with different molecular weights (12,000, 28,000, and 360,000 g/mol AppliChem GmbH, Germany CAS Number: 9003-39-8) was used to modify the polystyrene. Distilled water and butanol (CAS Number 71-36-3) and toluene (CAS Number 108-88-3) were used as degassing and modifying medium.

The release of the gas phase from the polystyrene foam samples was carried out in liquid media (water or butanol) in a special reactor and in the air media in a vacuum thermo-cabinet over a wide range of temperatures (333–390 K) and pressures (760–40 mmHg). The reactor is a cylindrical apparatus equipped with a heating jacket, a scraper stirrer (20–40 rpm), a screw conveyor and a solvent removal device. Vacuum thermo-cabinet is an apparatus equipped with a pump to create vacuum and heating elements to heat materials to a predetermined temperature.

The kinetics of degassing was studied by changing in the volume of EPS samples in different environments. Volume change (ΔV %) was determined on cubic or spherical samples at regular intervals and calculated using the formula:

$$\Delta V = \frac{V_i - V_t}{V_t} \cdot 100, \quad (1)$$

where V_i is the initial volume of the sample, m^3 ; V_t is the sample volume over time t , m^3 .

To obtain polystyrene-polyamide 6 materials, a mixture of polyamide 6 (Polyamide 6 PA-6-210/310 OST 6-06-C9-93 TU, RB 500048054.009-2001 JSC “Grodno Azot”, Belarus) with modified and degassed EPS (used household and industrial waste of EPS ASTM E2430/E2430M—19 with density 20–50 kg/m^3) was mixed in a viscous state on a Cellier laboratory extruder equipped with a screw of length of 700 mm and a diameter of 25 mm, followed cooling of the material in the form of a rod and grinding the resulting extrudate. The speed of screw rotation of the extruder is 10–15 rpm. The temperature in the zones of the extruder was 483–488, 498–503, and 513–518 K. The production of standard samples for research was carried out by injection molding on injection molding machine: Krauss Maffei KM 110–520 C2. The temperature in the zones of the material cylinder was 463–473, 478–488, 493–503, and 503–518 K. The content of modified polystyrene in PA 6 was 0–10 wt%.

The maximum sorption capacity of PVP by EPS was determined by gravimetric method and photocolormetry, which is based on the quantitative measurement of color of a complex formed by PVP with iodine. The method of determination is based on the formation with quantitative yield of colored complex PVP with iodine. The measurements were performed using a filter with $\lambda = 590$ nm. A solution of PVP in distilled water of known concentration was used to build a calibration graph of the dependence of optical density *versus* PVP concentration. For this purpose, cuvettes with a base number 2×10^{-2} m were used. One cuvette was filled with a solution containing 4×10^{-3} L PVP solution, 4×10^{-3} L 0.4 M; citric acid, and 5×10^{-3} L reagent solution obtained by dissolution 1.5×10^{-3} kg I_2 and 4.5×10^{-3} kg KI in 1.0 L of distilled water. Citric acid was added to maintain pH = 2.2 in which the resulting complex is more stable. The second cuvette was filled with a control solution with all reagents except PVP. The end of the photometer scale was adjusted on this cuvette, which automatically excluded the value of the cuvette and medium transmittance from the measurement results. After adjustment, the optical density of the working solution was measured. Measurement time is up to 10 min, as with longer use the solutions change their optical density. The Beer–Lambert–Bouguer law is implemented for PVP concentrations up to 0.1%. Knowing the weight of EPS and the amount of PVP in solution before and after sorption, the content of PVP in the sorbed samples was calculated. Measurements were carried out by a photocolormeter KFK-2 MP.

Along with the photocolormetric method, gravimetric method was used. The Sorption of PVP was carried out from alcohol and aqueous solutions at various temperatures and concentrations of PVP. The maximum sorption capacity W_s (g PVP/g EPS) was determined by the formula:

$$W_s = \frac{m_a - m_b}{m_b}, \quad (2)$$

where m_b is mass of EPS before sorption, g; m_a is mass of EPS after sorption, g.

To determine the apparent density, the polystyrene samples pre-conditioned at a temperature $(23 \pm 2)^\circ C$ and relative humidity $(50 \pm 15)\%$ until they reach a constant mass was used. Next, the linear dimensions of the bulk samples were determined with an accuracy of 0.5% and their weighting. Calculate the apparent density ρ_a , kg/m^3 , by the formula:

$$\rho_a = \frac{m}{V} \quad (3)$$

where m is the mass of the test sample, kg; V is the volume of the test sample, m^3 .

All results of studies determine the apparent density and sorption capacity are average values of at least three studies.

XRD analysis was used for determination of the effect of polystyrene wastes modified by PVP on the supramolecular structure of polyamide 6. X-ray diffraction patterns were recorded on DRON-4-07 diffractometer with an irradiating by lamp with a Cu-anode and a Ni-filter. (length of the light emitted $\lambda_{CuK\alpha} = 0.15418$ nm). The parameters of the lamp: $U = 40$ kV, $I = 30$ mA. Studies were conducted in the area of angles 2θ : 6° – 38° , the duration of the measurement step was 0.10, pulse measurement time 8 s.

The research results were processed by the WAXSFIT software [28], which is used to approximate the experimental diffraction curve, which corresponds to the variation of the X-ray scattering intensity (imp./s), depending on the diffraction angle 2θ . The approximation was performed using the Savitsky–Holey method and Pearson VII function. The application of this software allowed to determine the position of crystalline peaks and to optimize the process of decomposition of the diffraction curve into components using the Rosenbrock method.

The spectrograph SPECORD 70 was used for FTIR spectroscopy; the spectra were recorded within the range of 400 – $4,000$ cm^{-1} . Samples were prepared by pressing tablets with KBr.

Vicat softening point of the investigated materials was determined in accordance with ISO 306:2013B, the loading was 50 N.

The surface hardness of conical fluidity point was determined on Hepler Consistometer at 293 K by indentation of steel cone in the polymer sample with the sharpening angle of $58^\circ 08'$ under the load of 50 N for 60 s.

The tensile strength at break σ_{ts} , yield strength σ_{ys} , elongation at yield ϵ_{ys} , and elongation at break ϵ_{ts} were determined according to ISO 527-1,-2, using tensile testing machines TIRA Test 2200. The method is based on stretching the test specimen with a specified strain rate. Standard samples were used for the study. The strain rate was 50 mm/min.

All results of studies of physical-mechanical and thermophysical properties are average values of at least three studies.

RESULTS AND DISCUSSION

One of the main technological tasks for EPS waste modification is the selection of solvent for PVP that promotes the sorption process, since the nature of the solvent significantly affects the kind and capacity of sorption. It is known [29] that the adsorbent and solvent molecules in the process of sorption are competing with each other. The less solvent is adsorbed; the better is the sorption of the dissolved substance. At the same time, the sorption of a polymer is better when the solvent is more thermodynamically inappropriate.

The use of aqueous and alcoholic solutions for compression of EPS is caused by the technological possibility of polystyrene plastics modifying with water and alcohol soluble polymers with the simultaneous gas release, in order to improve some technological and operational characteristics or to provide them with specific properties.

In this regard, sorption was carried out in various solvents at different PVP concentrations. Taking into account that the temperature

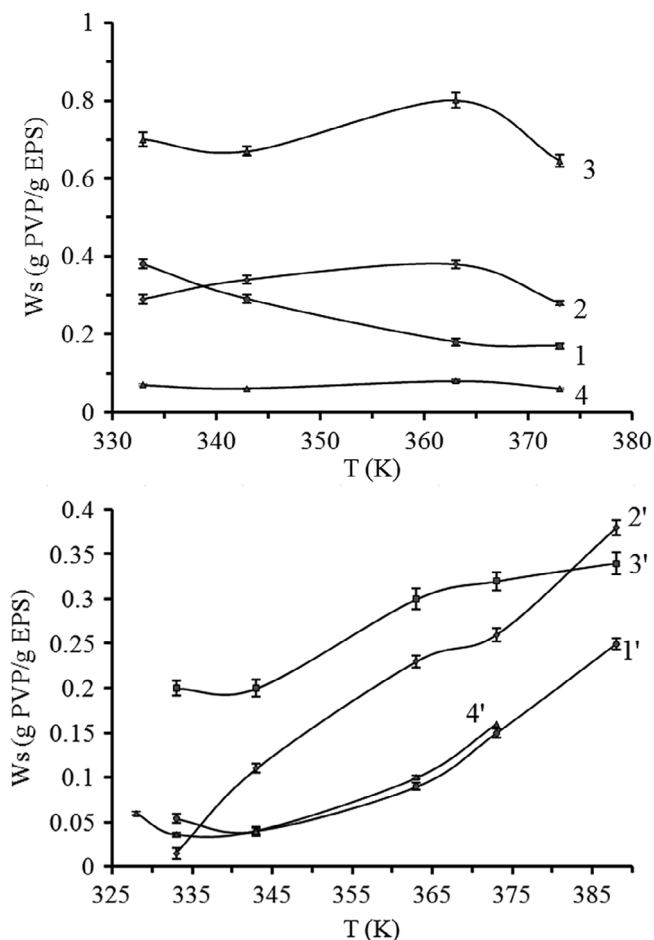


FIG. 1 Influence of temperature on the maximum sorption capacity of PVP on EPS depending on the PVP concentration. Solvent: 1, 2, 3—Water; 4—Water 90%-butanol 10%; 1', 2', 3'—Butanol; 4'—Butanol 90%-toluene 10%. $MM_{PVP} = 12 \times 10^3$ g/Mol. C_{PVP} , %: 1, 1'—1; 2, 2', 4, 4'—5; 3, 3'—10.

also affects the sorption mechanism, the investigation was carried out in a wide temperature range. From the technological point of view, taking into account the results of research on EPS densifying depending on the nature of the medium and temperature–time parameters, this temperature interval was chosen with regard to the peculiarities of the gas release. The obtained results are shown in Fig. 1.

Apparently (Fig. 1), the sorption capacity of PVP from aqueous solutions depends almost not at all on temperature. At the same time, the temperature of the process has a significant effect on the process of PVP sorption from butanol. In our view, this can be explained by a great affinity of the alcohol to the isopentane, which is present as a residue in EPS, and by a higher mobility of segments of polystyrene macromolecules in terms of polystyrene swelling caused by butanol. Along with the fact that at these temperatures there is an intense emission of the gas, which leads to a significant volume reduction, this promotes PVP macromolecules fixing in polystyrene samples.

The difference in sorption capacity from the aqueous and butanol solutions can be explained by the fact that in the water the PS surface does not swell, and this effect of temperature on the sorption capacity of PVP indicates the one-type process mechanism. The growth of sorption capacity from butanol and water at temperatures above

343 K is evidently caused by conformational changes in PVP macromolecules [30].

It should be noted that the effect of the solvent nature is also notable during the PVP sorption from binary solvents. Thus, the maximum sorption capacity from butanol-toluene solvents is lower than from pure butanol at temperatures up to 343 K (Fig. 1, curve 4'). At the same time, an increase in the toluene content up to 10% leads to a more sufficient decrease of the sorption capacity, which can be explained by a change in the conformations of PVP macromolecules in the boundary area and inside the solution volume, as well as by the concentration factor, namely, components redistribution in the system, resulting in the higher toluene content in the boundary layer compared with the entire volume. Since the butanol-toluene mixture is a thermodynamically worse PVP solvent than pure butanol, migration of PVP macromolecules from the border region is likely to occur. At higher temperatures, the mobility of solvent components increases, which promotes its uniformity throughout the entire volume, and thus leads to an impairment of its thermodynamic characteristics for PVP, which, as is known [31], increases the sorption capacity.

It is also worth noting that the effect of temperature on the PVP sorption from a water-butanol solvent is different than from the pure solvents, namely, there is some decrease in the sorption capacity with increasing temperature. This can be a consequence of the conformational changes in PVP macromolecules and the change of the thermodynamic characteristics of the solvent for PVP and EPS caused by the redistribution of intermolecular interactions in the system.

It is established that the maximum sorption of PVP is also strongly influenced by its concentration and molecular mass (Table 1).

As we see (Table 1), the sorption capacity of PVP from aqueous solutions significantly depends on the PVP concentration, especially for a PVP of relatively low molecular mass. Obviously, in this case, the structural parameters of the macromolecules, their flexibility induce not only the sorption on the surface of the EPS, as in the case of PVP with a molecular mass of 360×10^3 , but the penetration into the porous sorbent as EPS is. The optimal concentration of PVP in aqueous solution for PVP with a molecular mass of $12\text{--}28 \times 10^3$ g/mol is 0.8–1.2 base-mol/l, and for PVP with a molecular mass of 360×10^3 g/mol is 0.4–0.6 base-mol/l. At the same time, at temperatures which the most intense EPS compression occurs, the effect of the PVP concentration in butanol on sorption is independent of PVP molecular mass. Thus, the maximum sorption capacity for PVP with molecular mass of 12×10^3 g/mol and 28×10^3 g/mol is almost the same in a wide range of concentrations. In this case, the optimal PVP concentration in the solution is 0.4–0.5 base-mol/l.

TABLE 1. Influence of concentration and molecular mass of PVP on the maximum sorption capacity of compressed EPS.

PVP concentration (base-Mol/l)	PVP molecular mass (g/Mol)		
	12×10^3	28×10^3	360×10^3
	Maximum sorption capacity (g PVP/g EPS)		
0.1	0.080*/0.091**	0.081/0.105	0.080/0.141
0.45	0.380/0.232	0.280/0.250	0.280/0.170
0.9	0.819/0.300	0.720/0.274	0.360/0.182
1.1	0.920/0.319	0.805/0.280	0.375/0.184
1.4	0.950/0.325	0.828/0.282	0.395/0.185

* in butanol solution; ** in aqueous solution.

The presence of PVP as a modifier in degassed EPS samples is confirmed by the results of FTIR spectroscopy of EPS modified in butanol solution at different temperatures. The FTIR spectra are shown in Fig. 2.

First of all, the absorption bands characteristic of polystyrene are noted on the obtained FTIR spectra. In particular, the bands with the highest intensity are in the range $1,450\text{--}1,600\text{ cm}^{-1}$, which are characteristic of valence vibrations of bonds $C = C$ in the benzene ring and bands at $710\text{--}750\text{ cm}^{-1}$ correspond to C-H out-of-plane bending vibration absorption and indicate that there is only one substituent in the benzene ring, and bands corresponding to the deformation vibrations of the benzene ring (flexion C-H in the plane) at 1027 and $1,069\text{ cm}^{-1}$ [32]. In the case of modified polystyrene materials, displacements of typical PVP absorption bands were detected: $-\text{CH}_2\text{--}1450\text{--}1,550\text{ cm}^{-1}$, $\text{N--C} = \text{O}$ 1628 cm^{-1} , and $\text{C} = \text{O}$ 1677 cm^{-1} , indicating the presence of PVP in the modified material. In case of modification of PS at temperature 388 K (Fig. 2, curve 2) absorption peak of the group $\text{N--C} = \text{O}$ ($1,628\text{ cm}^{-1}$) is slightly more intense than at temperature 363 K, indicating more PVP adsorbed in the polystyrene material.

A slightly higher is the capacity of PVP sorption from the aqueous solutions compared with alcohol, which is especially manifested for more concentrated solutions. In our opinion, this is the result of a lesser compression of EPS samples in the aqueous medium, and, consequently, their higher specific surface and the system approach to reduction of interfacial tension between water and polystyrene due to sorption of PVP macromolecules on the surface (Fig. 3).

In the case of a butanol solution, the sorption capacity begins to grow (Fig. 3, curve 1') at the temperatures of the most intense degassing and does not depend on the surface area, which can be confirmed by the fact that the PVP sorption is mainly caused by the fixation of macromolecules inside the polystyrene being in swollen state in butanol.

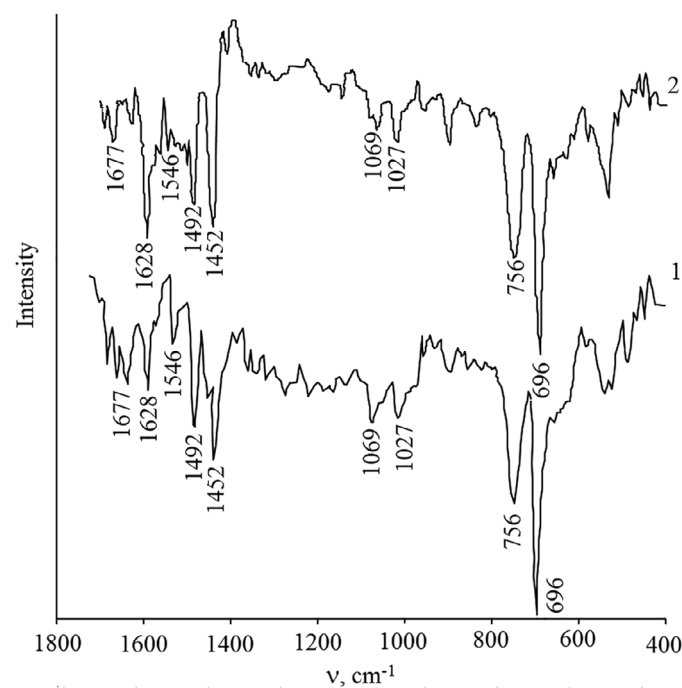


FIG. 2 FTIR spectra of EPS in PVP butanol solution at a temperature, K: 1–363, 2–388

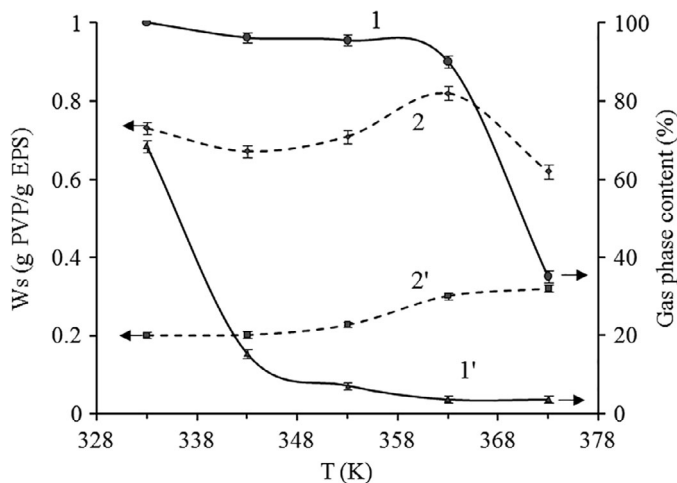


FIG. 3 Influence of the temperature on the maximum PVP sorption capacity and the EPS degasation level. PVP concentration—10 wt%. $MM_{PVP} = 12 \times 10^3$ g/Mol. 1, 2—aqueous solution; 1', 2'—butanol solution.

Thus, during the modification of EPS in butanol solutions of PVP, the optimum temperature of the process is ≈ 363 K, the dependence of the gas content on temperature is described by the equation:

$$W_{gf} = 0.87T^4 - 14.5T^3 + 88.1T^2 - 233.02T + 231.6; \quad (I)$$

and the dependence of sorption capacity on temperature is described by the following equation:

$$W_s = 0.0133T^3 - 0.16T^2 + 0.6467T - 0.56. \quad (II)$$

The given polynomial functions are obtained on the basis of experimental curves in the software environment CurveExpert 1.4.

Along with the detection of the influence of the medium nature and temperature on the PVP sorption by EPS, it was interesting to investigate the effect of the apparent density of EPS on sorption. The results are shown in Fig. 4.

As we can see, sorption decreases with the growth of the EPS apparent density and is described by the equation:

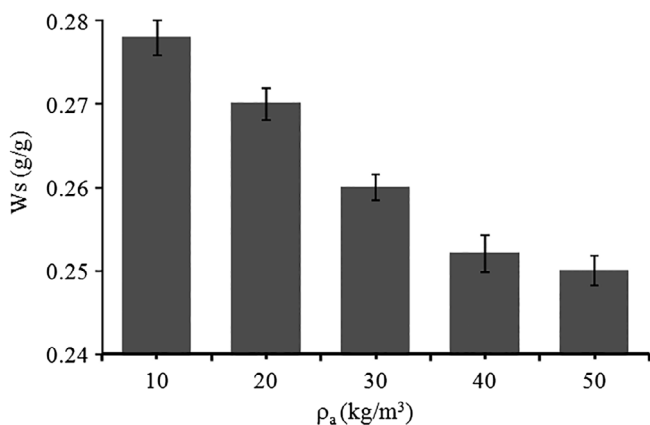


FIG. 4 Influence of EPS apparent density on the PVP maximum sorption capacity. PVP concentration—5 wt%; $MM_{PVP} = 28 \times 10^3$ g/mol; $T = 363$ K.

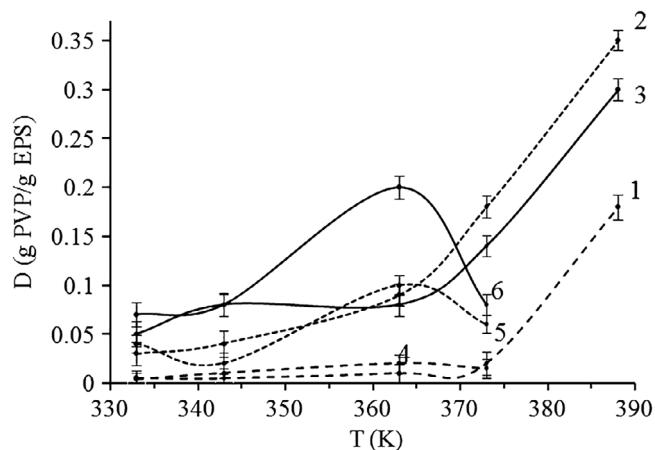


FIG. 5 Remaining content of PVP (D) after desorption in water of previously PVP modified EPS samples at different temperatures in butanol (1–3) and aqueous (4–6) solutions PVP concentration, wt%: 1, 4–1; 2, 5–5; 3, 6–10. $MM_{PVP} = 12 \times 10^3$ g/Mol.

$$W_s = 1 \times 10^{-5} \rho_y^2 - 0.0013 \rho_y + 0.2912. \quad (III)$$

Such a decrease in sorption with an increase in the initial packed density can obviously be attributed to the lower porosity of the EPS with a larger packed density. As a result the area of the active surface, on which sorption may occur, and the amount and size of the pores, in which fixation of the PVP macromolecules is possible, decrease.

The same sorption type in the case of all investigated PVP concentrations shows the same type of the dependence of the remaining PVP (D) content after samples washing off in water over a long period of time on the temperature at which sorption occurred (Fig. 5).

However, PVP sorption from butanol, unlike samples adsorbed from an aqueous solution, contain considerably more PVP after desorption. This can be explained by a change in PVP macromolecules conformations in a solution under the influence of butanol, and by greater interaction between PVP and polystyrene macromolecules as a result of PVP fixation in the polystyrene. It should be noted that as the increases of temperature and the concentration of the polymer increases the remaining content of PVP. The effect of temperature is more pronounced for butanol solutions of PVP.

Based on the revealed patterns of EPS compression, physical-chemical factors of influence on intermolecular interactions, conformational changes, flexibility and structural parameters of PVP macromolecules, as well as patterns of PVP sorption by EPS, rational parameters of polystyrene modification by PVP depending on the nature of the medium are proposed, which are given in Table 2.

Consequently, the obtained results prove to the effectiveness of the EPS modification with functionally active PVP with the simultaneous enhancement of the technological properties of the EPS due to the compression. It has been established that the compression of EPS samples and their PVP sorption depend heavily on the temperature, nature of the solvent, concentration and PVP molecular mass. In particular, the fastest degassing occurs in butanol or a mixture of butanol and toluene, but in these solvents the least sorption of PVP is observed. At the same time, the effect of PVP molecular mass on degassing time and sorption capacity are

TABLE 2. Rational technological parameters of the EPS modification process.

No	Solvent content (%)			$MM_{PVP} \cdot 10^{-4}$ (g/Mol)	C_{PVP} (base-Mol/l)	T (K)	τ (min)	Sorption capacity (g PVP/g EPS)
	Butanol	Water	Toluene					
1	-	100	-	1.2	1.0–1.2	363–373	20–25	0.95–1.00
				2.8	0.9–1.1			0.80
2	100	-	-	1.2	0.7–0.9	363–373	1–1.5	0.28
				2.8	0.4–0.5			0.27
3	10	90	-	2.8	0.4–0.5	353–363	10–15	0.18
4	90–95	-	5–10	2.8	0.4–0.5	333–343	1–1.5	0.12–0.15

negligible, with the highest values of PVP sorption and degassing time observed for the aquatic environment. At the same time, the use of a mixture of solvents, in particular butanol with water, can accelerate the degassing process and slightly reduce the temperature of the process, but there is a decrease in the sorption capacity.

The directional selection of the solvent and temperature enable predicted regulation of PVP sorption by EPS and, thus, affect the operational properties of the modified products.

Polymer blends with polyamide 6 were made on the basis of the modified EPS materials. On the basis of IR-spectroscopy (Fig. 6), significant changes in intermolecular interactions in polyamides under the influence of PVP-modified EPS were confirmed.

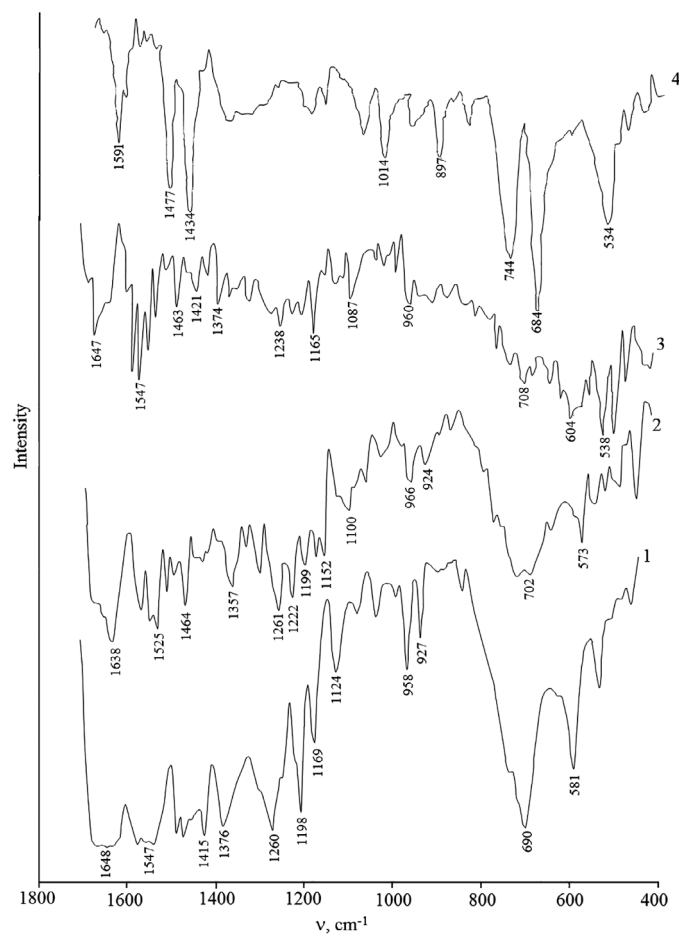


FIG. 6 FTIR spectra of the mixtures of PA-6—Modified EPS. Content of modified EPS, wt%: 1–0; 2–1; 3–2.5; 4–10.

In the spectrum of PA-6—modified EPS mixtures there are characteristic absorption bands of all its components, namely: amide groups—the bands with a frequency of $1,640 \text{ cm}^{-1}$ (Amide I) and $1,545 \text{ cm}^{-1}$ (Amide II) and bands assigned to PVP— $1,700$, $1,480$, $1,415$, $1,300$, and 650 cm^{-1} . The bands at 1600 , $1,492$, and $1,448 \text{ cm}^{-1}$ correspond to the vibration of the benzene ring, the band 752 and 696 cm^{-1} assigned to non-flat deformation vibrations of the CH-group in the benzene ring are characteristic of polystyrene. The band of Amide I corresponds to the stretching vibration of the group —C=O and the vibrations of different groups contribute in the Amide II band; however, the main contribution belongs to the deformation vibrations of the —NH— group [32] and these groups are responsible for the formation of intermolecular hydrogen bonds of the type —C=O... —NH— .

The growth of the intensity of the Amide I and Amide II bands and their shifting in the high-frequency area in the presence of a modified EPS indicates the formation of hydrogen bonds between the amide groups of polyamide and carbamate PVP groups, which provides the broader energy distribution of hydrogen bonds. For a blend compound with 10 wt% modified EPS, the absorption band expansion for Amide I and Amide II is so large that it can be assumed that a sufficiently developed spatial structure is formed by hydrogen bonds between amide and carbamate. Consequently, PVP, which is contained in a modified EPS, is actively involved in the redistribution of intermolecular hydrogen bonds in the polyamide to form new carbamate groups [33].

The influence of degassed and modified EPS on the physical-mechanical properties of PA-6 was determined (Table 3).

During the introduction of 1–2.5 wt% of degassed EPS yield strength practically disappears and the elongation at yield increases significantly. Along with this, the tensile strength at break changes slightly. Such features are most likely due to the fact that the introduction of degassed EPS leads to the destruction of intermolecular bonds between polyamide macromolecules, which, of course, will affect the supramolecular structure of polyamide 6 [22]. With a further increase in the content of degassed EPS, there is a decrease in both tensile strength at break and elongation at break, which obviously proves the thermodynamic incompatibility between the components of the mixture.

At the same time, the introduction of EPS modified by PVP leads to a decrease in ϵ_{ys} and to some increase in the yield strength at a constant value of elastic deformation. The decrease of elongation at yield with the increase of the content of modified EPS can also be explained by the formation of a denser structure due to the more advanced fluctuation network.

The investigation indicates that the nature and content of the polystyrene additive component significantly affects the morphological

TABLE 3. Mechanical properties of materials based on the PA-6—EPS blend.

EPS content (%)	σ_{ys} (MPa)	ϵ_{ys} (%)	σ_{ts} (MPa)	ϵ_{ts} (%)
0	55.5 ± 1.12	10 ± 0.5	53 ± 1.15	40 ± 1.3
1	55.5 ± 1.23*/41 ± 0.95**	13 ± 0.6/23.5 ± 0.9	50.5 ± 1.23/56 ± 1.11	30 ± 1.1/230 ± 3.6
2.5	60 ± 1.32/37 ± 1.03	13 ± 0.5/23 ± 0.8	51.5 ± 0.89/50 ± 1.3	28 ± 1.0/220 ± 4.3
5	57 ± 1.02/37.5 ± 0.96	12 ± 0.4/24.50.8±	49 ± 1.14/34 ± 1.08	22 ± 0.9/85 ± 2.3
10	55 ± 1.28/37.5 ± 1.06	11 ± 0.5/24.3 ± 0.8	48 ± 1.12/31 ± 1.32	13 ± 0.5/80 ± 2.2

* modified EPS; ** degassed EPS.

features of polyamide materials, primarily, the compatibility between the components of the mixture, which, along with the moisture content, is a key factor of the physical-mechanical properties of these materials. EPS modified with PVP, unlike the degassed sample, leads to some increase in strength parameters of PA-6, apparently due to higher compatibility between components of the mixture, which, in our opinion, is due to the intermolecular bonds redistribution under the influence of PVP [33].

Confirmations of the influence of EPS on the structure of PA-6 are the results of XRD analysis of the obtained materials. It is assumed that the effect of modified EPS, in contrast to the degassed EPS, on the polyamide 6 crystalline structure becomes apparent even at insignificant content in the mixture,

which is proved by the results of the XRD analysis shown in Fig. 7.

XRD analysis of mixtures based on PA-6 and modified EPS (Fig. 7) indicated the diffraction reflexes of PA-6 in the range of the diffraction angle $2\theta = 18\text{--}26^\circ$. In this case, the crystalline structure of PA-6 is formed by antiparallel packing of chains in the *ab*-plane due to the hydrogen bonds. Along the *c*-axis the chains are packed in parallel without hydrogen bonds. It should be noted that the diffraction reflexes of polyamide 6 with modified EPS differ from pure PA-6 in configuration of regions under diffraction curves. It is obvious that the nature of diffractograms of the modified EPS (2.5 wt%) significantly changes, in particular, the reflex of (002) α plane becomes considerably larger than the

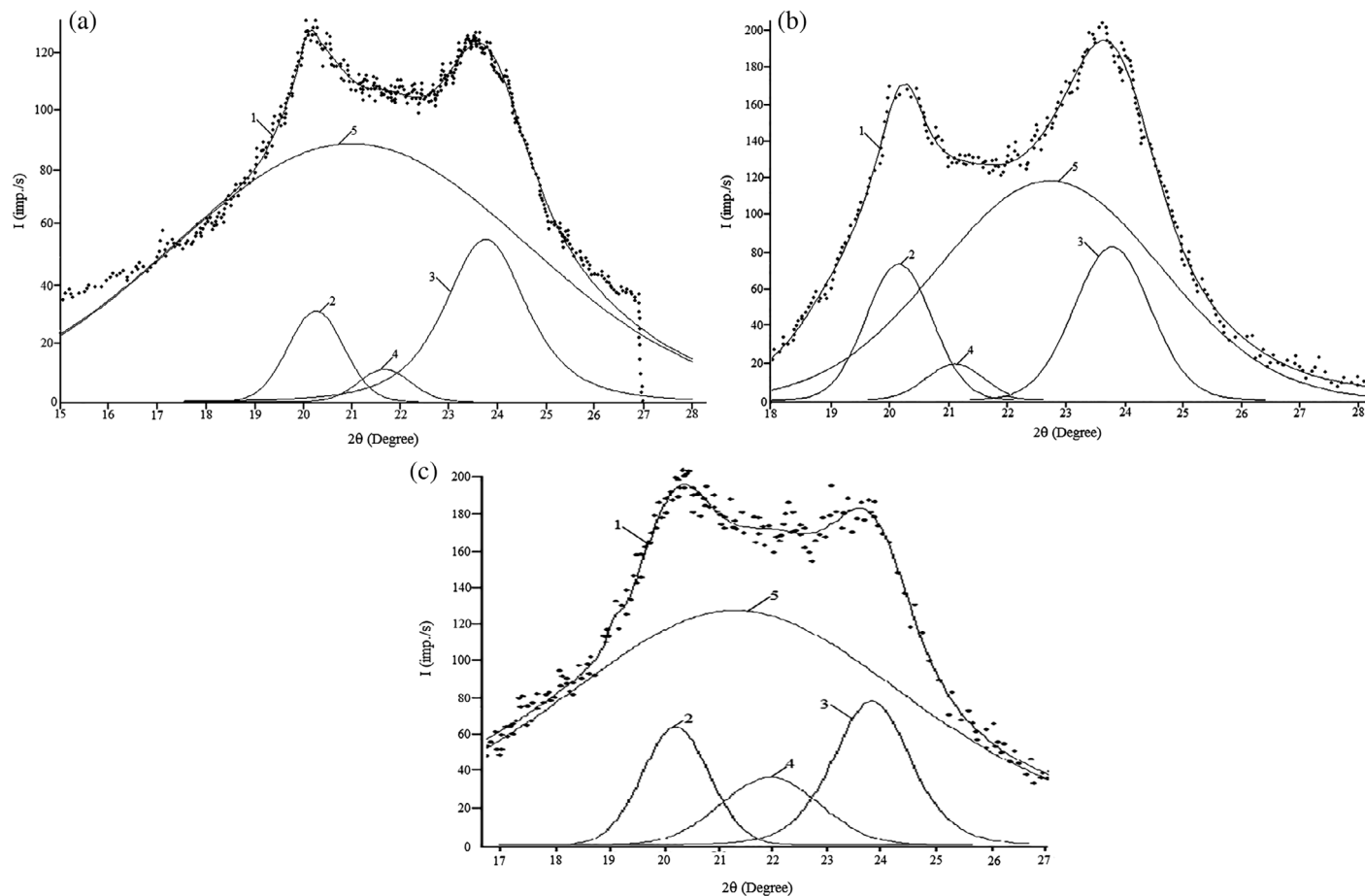


FIG. 7 XRD patterns of mixtures on the basis of PA-6 and EPS: (a) pure PA-6; (b) mixture of PA-6 and modified EPS; (c) mixture of PA-6 and degassed EPS. EPS content 5 wt%. 1—approximation curve of diffraction; 2, 3, 4, 5—optimized curves of intensity of reflexes of the planes (200) α -, (002) α -, γ -, and amorphous phase.

TABLE 4. X-ray structural parameters of materials based on PA-6.

Material composition, wt%	Plane	2θ , °	Height of peak	Width of peak	L^1_{hkl} , Å	L^2_{hkl} , Å	d_{hkl} , Å	S_c , %
PA-6—100%	(200) α	20.1	28.3	1.4	65.6	61.5	4.4	24.3
	(200) γ	21.4	8.3	0.6	159.4	149.5	4.2	
	(002) α	23.7	72.3	1.9	47.6	44.6	3.8	
PA-6–95%	(200) α	20.2	73.7	1.3	68.1	63.8	4.4	37.3
Modified EPS-5%	(200) γ	21.1	28.5	0.7	137.2	127.9	4.2	
	(002) α	23.8	82.8	1.5	58.8	54.5	3.7	
PA-6–95%	(200) α	20.1	67.3	1.2	71.2	66.9	4.4	31.2
Degassed EPS-5%	(200) γ	21.9	38.3	1.1	145.1	136.9	4.2	
	(002) α	23.9	78.9	1.4	64.2	61.3	3.7	

(200) α plane reflection, due to the effect of the modified EPS on the formation of the crystalline α -form PA-6. In addition, on the XRD pattern of 1–2.5 wt% modified EPS appears the reflex of the γ -phase of PA-6 at diffraction angles $2\theta = 22.5\text{--}23^\circ$, which is caused by a spatial network of hydrogen bonds [34].

Confirmation of these considerations is determined using the software package WAXSFIT [28] structural parameters of developed materials: the degree of crystallinity (S_c), crystallite size (L^1_{hkl} , L^2_{hkl}), interplanar distance (d_{hkl}) at the angle of crystalline diffraction peak (2θ), height and width of peak. The results are shown in Table 4.

It was found the introduction of degassed polystyrene, especially modified by PVP, into polyamide 6 leads to increase the degree of crystallinity of the material and reduce the crystallite size.

Surface hardness of mixtures of PA-6 with modified EPS increases (Fig. 8) with an increase in the additive content in the mixture, which is especially manifested in the mixtures with additive content up to 5 wt%. Obviously, this is the result of intermolecular interactions (mainly hydrophobic) of modified EPS with PA-6 macromolecules, which contribute to changes in the interphase layers and some mutual orientation of macromolecules with the formation of dense supramolecular structures resulting in the increase of surface hardness of the composite. In the case of degassed EPS, a decrease in surface hardness is observed, which may be caused by an increase in excess free volume [35], which is localized in the interphase regions, and by the increase of the system heterophasicity.

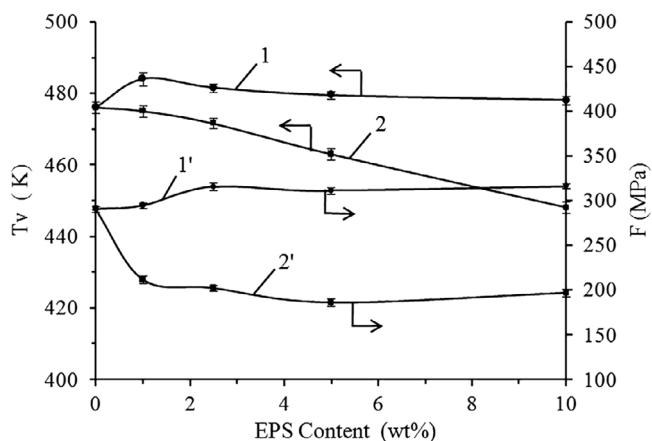


FIG. 8 Dependence of Vicat softening point (1, 2) and the surface hardness ($1'$, $2'$) of PA-6 on the content and additives nature: 1, $1'$ —modified EPS; 2, $2'$ —Degassed EPS.

It has been established that the nature of the modifying agent also has an effect on the thermophysical properties of modified polyamide materials. As can be seen in Fig. 8a, the influence of the additive's nature on the Vicat softening point of the modified materials is similar to that of surface hardness.

CONCLUSIONS

It is established that the rational method of EPS waste utilization is their degassing in the liquid state with the simultaneous modifying by PVP. This allows to apply them for creation of polymer composite materials based on blends of polyamide 6 and degassed EPS.

It was established that the EPS modifying by PVP during its degassing in liquid media occur due to the sorption of PVP macromolecules, which contributes to their uniform distribution at the molecular level in the polystyrene matrix. It was found that the sorption capacity depends on the nature of the solvent, temperature of the process, concentration and molecular mass of PVP. The rational technological parameters of modifying process and compressing of the EPS (the medium is a 5% butanol solution of PVP, temperature—363 K, time—1–1.5 min) is established.

Increased compatibility in viscous-flow between the polyamide 6 and the modified EPS is caused by the uniform distribution of PVP macromolecules in the polystyrene matrix and intermolecular interactions between the functional groups of PVP and polyamide 6. It was confirmed by instrumental analytical methods (XRD, FTIR spectroscopy). It was found that 1–4 wt% of modified EPS increases the yield strength, surface hardness and Vicat softening point of polyamide 6 by 5%–10%.

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