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APPLICATION POTENTIAL OF MIXED POLYMERIC WASTES OF ACCUMULATOR BATTERIES FOR ARTICLE MOULDING

The composition and properties of mixed polymeric wastes of accumulator batteries have been determined. The possibility of waste processing into moulded articles by pressing with pre-plastication has been ascertained. Physical and mechanical properties of materials from mixed polymeric wastes have been defined. Recommendations on the regimes of waste processing suitable in terms of their technological and technico-economic parameters have been worked out.

Introduction. One of the promising ecological projects implemented at JSC "Beltsvetmet" is processing of spent automobile accumulator batteries. Modern Italian equipment for mechanical fractionation of batteries was put into operation at the end of 2009.

The batteries are processed with electrolytes, electrolytes being recovered at all stages of production. Nearly 5,600 accumulator batteries were utilized in 2010. Nowadays electrolytes are accumulated and lead is used for the production of new accumulator batteries. Mixed polymeric wastes which are not used anywhere today are formed in the course of battery processing. Production of useful articles from such wastes is ecologically and economically favourable, though there are some difficulties.

The wastes contain thermoplastic and thermosetting polymers which may include sulphuric acid and lead and are thus dangerous for the environment. Waste processing technology must exclude negative influence on the environment and living organisms.

Traditional methods of injection moulding and extrusion are ineffective for waste processing due to nonuniformity of composition and high melt viscosity. Technologies which are effective for the processing of mixed polymeric wastes into useful articles are: pressing of articles from plasticized compounds, and plastic moulding [1].

The process of producing moulded articles from initially plasticized compounds includes: preparation of feed stock (washing, drying, reducing and (if necessary) classification of mixture components); batching and packing of a compound; smearing in a rubber extruder; accumulation of plasticized material; formation of an extruded stock; transfer of an extruded stock to the mould and pressing of an article.

The aim of the research is to assess the conditions of mixed polymeric waste processing of accumulator batteries and the spheres of application of moulded articles.

Main part. The composition of mixed polymeric wastes of accumulator batteries (PWAB) has been investigated. Sample weights of 150 g by mass were selected from the original stock of reduced wastes.

The sample weights were identified in terms of density, melting point and behavior in conditions of direct flame [2, 3]. The content of mixture components was defined by weighing on the laboratory scales within the accuracy of 0.1 g.

pH of PWAB aqueous extracts as well as that of the secondary polypropylene (ground accumulator battery jars (ABJ) have been defined.

The sample weight of 2 g by mass was placed into the reservoir with distilled water (100 ml by volume), was being kept there for 2 hours after which its pH was measured.

ABJ were added to PWAB in the mass ratio 70 : 30 and 50 : 50. The obtained mixtures were being initially dryed at 80ºC for 2 hours and plasticized in a screw extruder 32×25.

The zone temperature was chosen proceeding from the processing temperature of thermoplastic components of a mixture. The dose of plasticized material was prepared in a heated storage unit (accumulator).

The processing rate was determined by the time of material dose accumulation. The storage density of plastication was calculated in terms of the processing rate and amount of the consumed electric energy.

The plasticized preform was pressed in a cool mould (250×250 mm) under a force of 150×300 kH, the thickness of the resultant plates being 4–6 mm.

Preform temperature and shape-generating form surfaces were controlled by infrared noncontact thermometer "BYM". Special samples were cut from these plates to determine the characteristics of technological and physical and mechanical properties.

Sulpha and lead content in the original samples of PWAB as well as in moulded articles was determined by scanning electron microscopy method (СЭМ) using scanning electron microscope JSM-5610LV with chemical analysis system EDXJED-2201 JEOL (Japan).

Consistency index and power exponent were determined by pressing the disk between plane parallel plates heated above melting point [1].

Thermal diffusivity was determined proceeding from temperature time interval (50 ± 0.5)ºC in the centre of a rectangular cross-section sample, the latter being heated between plane parallel plates (plate temperature (100 ± 1)ºC). The density was determined according to GOST 15139-69.

The ultimate flexural strength was determined according to GOST 4648-71, the modulus of elasticity – according to GOST 9550-81. The samples were loaded according to a three-point connection.The distance between plate supports was 60 mm, the speed of loading at determining modulus of elasticity was (2 ± 0.5) mm/min, and the speed of loading at determining the ultimate flexural strength was (20 ± 2) mm/min.

Diagrams of sample deformation were recorded. The modulus of elasticity was determined under deformations up to 0.5%. The modulus of elasticity was determined as a mean value of not less than three samples, and the ultimate flexural strength was determined as a mean value of not less than 5 samples.

Stress at break and modulus of elasticity were determined according to GOST 11262-80. Not less than five samples were tested to determine the stress at break and up to three samples – for determining the elasticity modulus.

Shearing strength was determined according to GOST 17302-71 and flexural impact stress – according to Gost 4647-80.

Initial mixture components of the reduced wastes and their mass content are shown in Table 1. It is ascertained that PWAB consist of components which don't melt during plastication process (up to 70 wt %), i. e. they are used as fillers, and a mixture of thermoplastic polymers (up to 30 wt %).

Table 1

Components of waste mixture and their mass content

Mixture components	Mass content
Ebonite (solid rubber)	17.4
Polypropylene	15.4
Lead	8.2
Polyamide	7.5
Batting	5.3
ABS -plastic	4.2
Polyethylene	1.8
Others	39.2

Large amount of a filler results in the increase of melt viscosity, makes the moulding process more problematic and requires more power for plastication and mixing of components. It may also lead to a considerable nonuniformity of materials in the finished product [4]. That is why the addition of a thermoplastic polymer into the PWAB is of great necessity for the improvement of moulding conditions. For this purpose 30 and 50 wt % of the secondary polypropylene extracted in the process of ABJ grinding were added to the initial mixture.

The regimes of compound processing are shown in Table 2. The greater part of the mixture of thermoplastic polymers consists of polypropylene, that is why temperature regimes of plastication were set in terms of the temperature range characteristic for its processing.

The productivity of the plastication process is 19 kg/h in average. But the PWAB + ABJ compound resulted in a large range of productivity (coefficient of variation being 20%) and this testifies the nonuniformity of a composition and viscous properties. Besides, the productivity of the plastication process for the given compound is 10% less in average than for the PWAB + ABJ compound (50 : 50). The total energy density of the plastication and moulding processes is not more than 1 kWh/kg. This parameter is much less than the one for injection moulding and extrusion. The energy density of the PWAB+ABJ (50 : 50) mixture plastication process is 0.1 kWh/kg lower than that of PWAB+ ABJ (70 : 30) in average.

The pressing of the PWAB+ABJ (70 : 30) compound needs moulding force of 100-150 kH and higher in average. Indexes of technological and physical and mechanical compound properties are shown in Table 3. The higher the temperature, the lower the consistency coefficient. Consistency coefficient of PWAB + ABJ (70 : 30) compound is higher than that of PWAB + ABJ (50 : 50) compound. Both compounds are suitable for processing using plastic-moulding method. Moulding of articles from PWAB + ABJ (70 : 30) compounds needs more moulding force, and this was proved by the experiment.

Table 2

Regimes of compound processing from mixed thermoplastic wastes of accumulators by plastic-moulding method

Parameter		Parameter value for the compound	
		PWAB+ABJ (50 : 50)	PWAB+ABJ (70 : 30)
Temperature in extruder sections, ºC	I	200	200
	II	220	220
	III	240	240
Velocity of screw rotation, rev/min		185	185
Accumulator temperature, ºC	IV–V	240	240
Energy density, kWh/kg		0.75/21%	0.81/21%
Productivity kg/h		20.7/6%	18.6/19%
Preform temperature, ºC		220	225
Mould temperature, C		20–35	20–35
Moulding force, kH		200	300
Dwell time, min		1.5	2.0
Temperature of a finished article, ºC		55	60

Notes. Numerator – average value; denominator – coefficient of variation.

Elastic modulus, stress at break and stress in bending differ slightly, i.e. the presence of ABJ practically doesn't affect mechanical properties of compounds. The index range is little (coefficient of variation is not higher than 10%), and this proves relative uniformity of the compounds post plastication.

The tensile and bending strength indexes as well as impact resistance are 1.5–2 times lower than those specified by the regulations for thermoplastic components. It is obvious that lower compound strength in comparison with the strength of its thermoplastic components is due to not very strong bonds between the structural elements in materials produced from the mixture of components. It is proved by the brittleness of samples from mixed wastes and by high indexes of shearing strength. The samples rupture without neck formation under tension. Diagrams of tension are linear almost till rupture occurs (see Fig. *a*).

Under bending rupture occurs in the tension section. Typical diagrams of deformation under bending are shown in Fig. *b*.

In conditions of intensive mixing action and the ABJ content not less than 30 wt %, the hjghjthermoplastic polymer encapsulates particles containing lead oxides and sulphuric acid. The content of sulphur and lead in the surface layer of samples from PWAB is determined by the SEM method. This content is in the limits of 1 wt %.

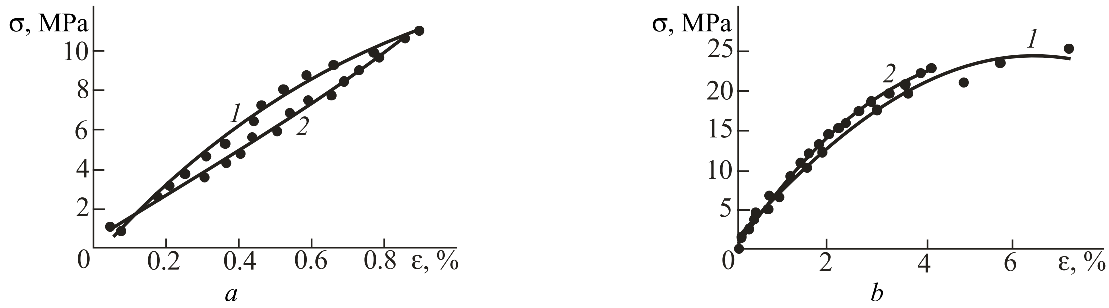
Taking into account the data from Table 3 and the behaviour of materials from mixed polymeric wastes during tests, and considering the resultant colour of the preforms post plastication (grey) we have defined spheres of probable application of articles produced from them. These are preferably flat, dark-coloured articles. No strict requirements are imposed on toughness, strength and surface quality of these articles. The articles are used in production rooms, storage rooms, utility rooms or underground where the influence of climatic or atmospheric factors is limited. These articles may be of minor assignment for the usage in the environment e.g. for setting up the territory. Examples of such articles are as follows: paving slabs for the floors of production rooms and garden paths, trays, concrete moulds for the paving slab production, plant bands, elements of the area improvement, packing material, etc.

Table 3

Indexes of technological and physical and mechanical properties of compounds

Index		PWAB + + ABJ (50 : 50)	PWAB + + ABJ (70 : 30)
Consistency coefficient,	200°C	21.5	24.6
	240°C	20.0	20.9
Flow rule index	200°C	0.35	0.34
	240°C	0.56	0.29
Thermal diffusivity, mm²/s		0.12	0.13
Density, g/sm³		1.16	1.26
Failure strees in bending, MPa		25.2	21.7
Flexural modulus, GPa		1.3	1.7
Stress at break, MPA		10.6	11.1
Tensile modulus, GPa		1.6	1.6
Shearing strength, MPa		20.6	17.7
Charpy modulus of resilience, kj/m²		12.3	9.8

Conclusion. 1. Mixed polymeric wastes of accumulator batteries (PWAB) contain a large portion of non-fusible components – about 70 wt %. Plastication and moulding conditions are improved if they are added with wastes of the accumulator battery jars (ABJ) in the amount not less than 30 wt %.



Diagrams of deformation of PWAB+ABJ mixtures under tension (*a*) and bending (*b*):
1 – (50 : 50); *2* – (70 : 30)

Due to the productivity and energy density criteria it is preferable to use compounds with the ABJ content equal to 50 wt %.

2. Recommendations on the regimes of waste processing which are suitable in terms of their technological and technico-economic parameters have been studied and developed experimentally.

3. In conditions of intensive mixing action in the extruder and the ABJ content not less than 30 wt %, thermoplastic polymer encapsulates particles containing lead oxides and sulphuric acid, and this nearly eliminates their harmful effect on the environment.

4. On the basis of the results of mechanical tests we may conclude that the examined compounds are applicable for the production of articles which are not affected by excessive load and can be used in conditions where the influence of climatic or atmospheric factors is limited.

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