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Highly filled polyethylene/barium metaplumbate composites for lead acid bipolar battery application

RAPID COMMUNICATION

Summary — Barium metaplumbate (BMP) is proposed as a conducting filler of polymer composite materials, used for production of support of active materials in lead acid bipolar battery. The composites of BMP with polyethylene as a matrix polymer, were prepared by means of Brabender kneader mixer were the PE matrix was modified by an addition of a liquid crystal polymer PET/PHB with the aim to regulate the matrix viscosity. The BMP content in the composites was in the range between 92 and 94 wt. %. The electrical resistivity of the composites was found to be significantly dependent on BMP content, and an increase of the Vicat temperature was also observed for the composites. A homogeneous distribution of the barium methaplumbate particles in the polyethylene matrix was established by the SEM observation.
Key words: barium metaplumbate, lead acid bipolar battery, polymer composite, electrical resistance, Vicat temperature.

WYSOKONAPEŁNIONE KOMPOZYTY POLIETYLEN/METAOŁOWIAN BARU DO ZASTOSOWAŃ W BIPOLARNYCH AKUMULATORACH KWASOWO-OŁOWIOWYCH

Streszczenie — Metaołowian baru (BMP) jest jednym z materiałów proponowanych jako napełniacz przewodzący kompozytów polimerowych, wykorzystywanych do produkcji nośnika materiału elektrodowego akumulatora kwasowo-ołowiowego o konstrukcji bipolarnej. Kompozyty metaołowianu baru i polietylenu jako matryce polimerowe, wykonano wykorzystując plastograf Brabendera. Matrycę polietylenową modyfikowano poprzez dodatek polimeru ciekłokrystalicznego PET/PHB w celu uzyskania właściwej lepkości. Zawartość BMP wynosiła od 92 do 94 % mas. (tabela 1). Ustalono, że opór właściwy kompozytów maleje ze wzrostem zawartości BMP (rys. 3). Wysoki stopień napełnienia spowodował również wzrost temperatury mięknienia według Vicata. Na podstawie obserwacji SEM stwierdzono jednorodność rozproszenia ziaren metaołowianu baru w matrycy polimerowej (rys. 4 i 5).
Słowa kluczowe: metaołowian baru, bipolarny akumulator ołowiowo-kwasowy, kompozyt polimerowy, opór właściwy, temperatura mięknienia według Vicata.

A bipolar lead-acid battery is known to be advantageous over the conventional monopolar battery in terms of power output. A schematic diagram of a bipolar battery is shown in Fig. 1 [1]. The most important part of a bipolar lead battery is the support of the active material. In a bipolar configuration the active material is placed on the opposite side of the substrate.

The material for the substrate of a bipolar lead-acid battery must fulfil the following requirements: a good conductibility, an insolubility in a sulfuric acid, a high oxygen and hydrogen over potential, should be inert to battery reactions, must present a good adhesion to the battery active materials, should be a low cost material, and finally ought to prevail a lower density in comparison with lead [2].

The barium metaplumbate ($BaPbO_3$, BMP) may be used as a conductive filler. This product is also proposed as an additive for the active material which improves the efficiency of a battery formation [3, 4]. The BMP prevails also a good electrical conductivity of the metallic type, and it's electrical resistivity at 25 ^oC is of the order of $8.3 \cdot 10^{-4}$ ohms [5]. Because of its specific characteristics the BMP is proposed as a material to produce some types of electrodes, for example to produce ozone, or for electrolytic synthesis of manganese dioxide [4], and also as a support to bipolar batteries [4, 6].

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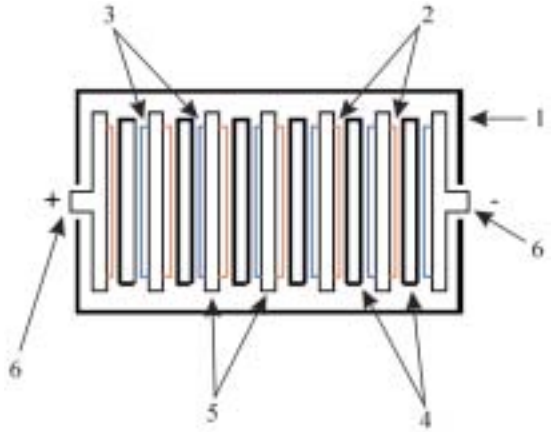

Fig. 1. Cross-section of a bipolar lead-acid battery: 1 — container, 2 — positive active mass (PAM) on one face, 3 — negative active mass (NAM) on the other face, 4 — glass fibre separator, 5 — support, 6 — monopoles

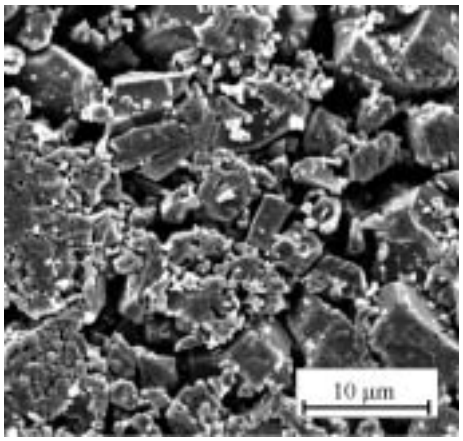

Fig. 2. SEM photo of barium metaplumbate (BMP)

The polymer composites with a conductive filler are proposed as good candidates for the bipolar substrate. In this case a composite of polyolefins with BMP seems to fulfil the conditions necessary to act as a support of an active material of a bipolar battery [6].

The main task of this work was to produce a homogeneous mixture of a polyethylene with a high content of the BMP, *e.g.* to create a composite with as great as possible number of direct contacts between the fillers particles. In this case the thermoplastic polymer should play simply a role of a matrix, allowing to fabricate parts of a battery with various shape.

EXPERIMENTAL

Materials

Preliminary substrates used for the synthesis of BMP were lead nitrate [$Pb(NO_3)_2$, POCh Gliwice, Poland] and barium hydroxide [$Ba(OH)_2 \cdot 8H_2O$, POCh Gliwice, Poland]. The solid state mixtures, prepared in concentration Pb:Ba = 1.3:1, were placed in the high temperature oven and heated at 780 ^oC during 1 hour. To obtain a homogenous distribution of BMP, with particles mean dimension lower than 0.06 mm, all samples were pulverized after cooling.

On Figure 2 the morphology of BMP particles is presented. As it may be seen as well small as larger grains, of an irregular form, are produced as a result of a high temperature synthesis of BMP, followed by grinding.

As a matrix polymer a high density polyethylene (PE-HD, trade name Rigidex HD5226E) produced by BP Solvay Polyethylene Europe, was used. The composites of BMP with polyethylene, were prepared by means of Brabender kneader mixer, blended in a molten state by a temperature of 170 ^oC; the processing time was 10 min. The BMP powder content in the composites was 92, 93 or 94 wt. %, respectively.

Since the composites were prepared with a very high BMP powder content, a prior modification of the viscosity of the matrix polymer was necessary [7]. For this reason the liquid crystal polymer (LCP), produced by Unitika Ltd. [copolymer of poly(ethylene terephthalate) and 0.6 mole fraction of *p*-hydroxybenzoic acid], was introduced into the matrix polymer [8, 9] by melt mixing, allowing to achieve a required melt viscosity of the blend. The LCP content was in the range between 10 and 40 wt. %.

Methods

To characterize the thermal properties of these highly filled composite the Vicat temperature was measured according to standard PN-EN ISO 306.

The determination of the electrical resistivity of the polymeric composites was realized with a specially constructed device [10]. The compacted samples, with a diameter of 6.5 mm, were placed in a PMMA tube, and charged with a constant load of 700 N. Both ends of the sample were in a permanent contact with the electrodes. The current of 100 mA passed through the sample, and the respective voltage drop was recorded.

To evaluate the specific electrical resistivity of the investigated material the measured resistance value was multiplied by the surface area of the sample and divided by its height.

The scanning electron microscopy SEM observations were performed on the surface and on the cross section of the compressed blends.

RESULTS AND DISCUSSION

Vicat thermal resistance

The results of the Vicat temperature measurements, for blends with various composition, are presented in Table 1. As it may be seen, generally the addition of the BMP to the PE-HD/LCP composition results in a higher thermal resistance, comparing with the pure polyethy-

T a b l e 1. The Vicat temperature for PE-HD/LCP composites

PE-HD/LCP weight ratio	BMP content wt. %	Vicat temperature °C
100:0	0	133
80:20	92	143
80:20	93	146
80:20	94	143
70:30	92	148
70:30	93	142
70:30	94	145
60:40	92	141
60:40	93	143

lene Rigidex HD5226E, where the increase was in the range between 8 to 13 deg. The differences in the thermal resistance, observed for the composites of PE-HD/LCP with BMP, may be related to the inhomogeneity of the material, as well to the specific measurement method. It's known that in the case of the Vicat temperature measurements the pine needle penetrates the surface of the sample, and specially in the case of highly filled composite the result depends on the situation if the needle touches the matrix or the filler particle.

Electrical resistivity

Figure 3 presents dependence of specific electrical resistance on BMP content.

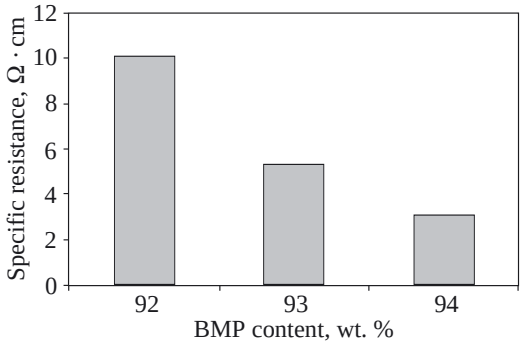

Fig. 3. Effect of BMP content on specific electrical resistance of the blend

The lowering of the electrical resistivity, with increasing BMP content may be probably related to the rising number of contact points between the surfaces of BMP particles. This effect confirm the possibility of replacement of the lead plates in batteries by investigated composites.

Morphology

As it was shown in Figure 4 the SEM photographs of the surface area of the composites allows to detect that a nonconductive polyethylene film is created as a surface

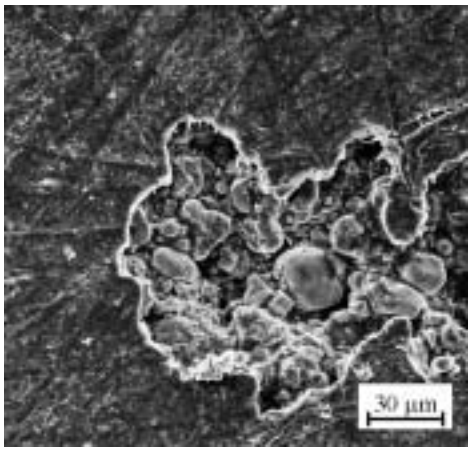

Fig. 4. Surface of the composite with 94 wt. % content of BMP

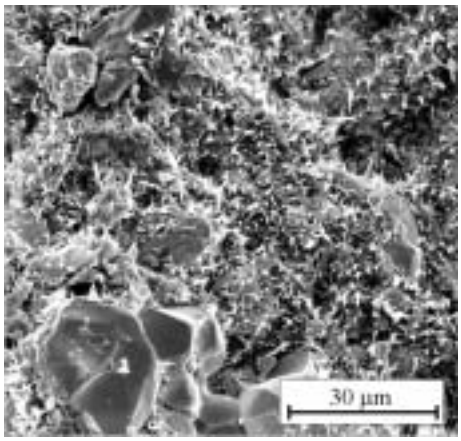

Fig. 5. Cross-section of the composite with 94 wt. % content of BMP

layer of the plates-form samples during preparations by compression molding. This effect may explain the relative high value of the electrical resistivity of the composites, as presented before. However, in some parts of the surface area the BMP grains directly may be seen. This indicates that for improvement of the electrical conductivity a special surface treatment, giving a direct access to the conducting material, has to be applied [11].

On the contrary, on the cross section (Fig. 5) a homogeneous dispersion of the BMP grains in the PE-HD/LCP matrix was observed. Similarly, like for pure BMP, a random distribution of irregular smaller and bigger grain may be seen in this case.

CONCLUSIONS

It was found that as a result of melt mixing of a high content of barium metaplumbate with PE-HD/LCP matrix, a composite material with specific properties may be prepared. Comparing these results with special electrochemical investigations [12] it may be stated that this highly filled composite may serve as a support of an active material of a bipolar lead acid battery.

A relative high value of the electrical resistivity of the composite may be attributed to the creation of a nonconductive layer of pure polymer on the composite surface. Therefore, further work will be focused on the modification of the surface, with the aim create layer with a good electrical contact.

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