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Foamed poly(lactic acid) composites with carbonaceous fillers for electromagnetic shielding

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ABSTRACT

Electromagnetic shielding is one the key factors for electronic devices in their use and transportation. Polylactide (PLA) is a biodegradable polymer with a moderate biodegradability and decent mechanical properties. Replacement of traditional materials by biodegradable polymers brings about the fossil resources savings and helps solving problems related to the plastic packaging waste. In this work composites of PLA with carbon black and carbon nanofibers were described. Improvement of the material mass/electromagnetic interference SE (shielding effectiveness) ratio can be obtained by introducing foaming technology into the material preparation process. Microporous structure can greatly improve material properties such as thermal isolation, mechanical properties and in case of composites filled with carbonaceous fillers such as carbon black carbon fibres – also the electrical conductivity.

In order to improve their application range and reduce density, a cellular structure was created using chemical blowing agent. It was found that in low loaded composites (although above the percolation level) the shielding effectiveness relies on the amount of a conductive filler but it may be additionally enhanced by the foaming process. Electrical properties, electromagnetic shielding effectiveness and morphology of cellular composites for described polymer-filler systems have been presented.

1. Introduction

In modern world full of the electronic hardware one of the most important but least noticeable issue is a need to shield the electric devices from electromagnetic interferences (EMI). Electric devices emit electromagnetic fields at various frequencies, which can cause a significant damage or poor performance of the equipment. Electromagnetic shielding can be addressed to the reflection and/or absorption of electromagnetic radiation by a material. Reflection is regarded as a primary shielding mechanism and in order to perform shielding, the shield must interact with electromagnetic fields in the radiation due to mobile charge carriers. Secondary shielding mechanism – absorption, is realised by electric or magnetic dipoles that interact with electromagnetic fields in the radiation [1]. Therefore the shielding materials use to be conductive and the most commonly they are metals. Although conductivity is not necessary, it is advisable when shielding electronic devices. Electromagnetic radiation, especially that of high frequencies tends to interfere with electronics such as computers, containing many microchips that can be harmed due to electrostatic discharges. Packaging/shielding material should be able to protect viable electronic goods both from the electromagnetic radiation and accidental electrostatic discharges. Both criteria meet metals but they are bulky and expensive in transportation. Polymer composites filled with electrically conductive carbon based materials (carbon black – CB, carbon nano fibers – CNF, carbon nanotubes – CNT) are by far lighter and easy to manufacture. In comparison with metals, polymer composites are semiconductors, but for good antistatic properties with a charge dissipation half-time of 2–10 s the surface resistivity of 10^{10} – 10^{11} [Ω cm] is required [2]. Such resistivity can be obtained for electroconductive polymer composites with most of the common fillers at a volume concentration close to the percolation threshold [3–7].

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Further improvement of the material mass/EMI SE (shielding effectiveness) ratio can be obtained by introducing foaming technology into the material preparation process. Microporous structure can greatly improve material properties such as thermal isolation, mechanical properties and in case of composites filled with CB or CNF – also the electrical conductivity [8–10]. Filler particles have less polymer volume to occupy which allows to obtain lower percolation threshold when compared to conventional solid composites. Polymer foams with carbon-based conductive fillers can be an alternative to currently used materials, such as high cost conductive polymers. They combine low weight and good EMI shielding with low cost and can be tailored for specific applications [11–15]. Zhang et al. [16] developed a novel composite material consisting of a syntactic foam (hollow carbon microspheres in resole resin) reinforced with CNF. The filler content was 0.7; 1.4; 2.1 and 2.8 vol.%. The composite preparation took place in a high-shear homogenizer and the shielding effectiveness was evaluated as a ratio between the incoming and outgoing power of an electromagnetic wave. Maximum EMI shielding was ca. 25 dB for a composite containing 2.0% of the filler. Ameli et al. [17] presented composites with a polypropylene matrix, filled with CNF for EMI shielding. Their work focused on the effect of foaming on the carbon fibers orientation, aggregation and on the percolation threshold. The EMI SE was measured in the X-band frequency range (8.0 – 12.4 GHz). They observed that a physical foaming of PP-CF composite caused a change in its microstructure due to the biaxial stretching of cells with the fibers and by the plasticizing effect of a dissolved gas on the viscosity of composites. Also the density of composites was reduced by 25% as a result of foaming. Electrical properties were also improved due to higher fibers inter-connectivity as a result of the biaxial stretching during foaming. The percolation threshold was reduced from 8.75 to 7 vol.%, while EMI SE increased for over 65%.

Biopolymers have attracted recent years a great attention for replacing the petrochemical based plastics due to the fossil fuel depletion, ecological hazards by the non-degradable plastics and an overall public concern. One of the most widely used alternative for conventional plastics is polylactide (PLA) which has good mechanical properties (similar to polystyrene), is fully biodegradable, biocompatible, of good chemical resistance and derived from renewable resources (e.g. corn starch). It can be processed with conventional processing methods (injection moulding, extrusion, spinning and others) [18,19]. Range of applications varies from medicine implants and compostable packaging, to agriculture. When developing a novel packaging material for EMI shielding one has to take in mind the ecological aspect of such. Packaging has a very short life span and tends to be discarded soon after use and according to the best knowledge of the authors there are no papers concerning implementation of biodegradable polymers for EMI shielding material.

Therefore the aim of the work reported was to develop a lightweight biodegradable polymer composite filled with cheap conductive filler mainly for packaging application, with good EMI SE properties along with ability to protect from electrostatic discharges, combining good mechanical and functional behaviour with low density.

2. Materials and methods

2.1. Materials

Composites were prepared by melt mixing of polymer matrix, PLA 3052D from NatureWorks, with carbon based fillers. Mixing was performed using a Thermo Scientific Polylab QC equipped with internal mixer with chamber temperature of 180 °C and rotor speed of 60 RPM. First was carbon black (CB) Ketjenblack EC-300J from Akzo Chemicals which according to manufacturer specifications has a very high specific surface area (approx. 800 m^2/g (BET)), low ash content and apparent bulk density of 125–145 kg/m^3 Second filler constituted nanosized carbon nanofibres (CNF) PR-19XT-HHT from Pyrograf Inc. According to the producer their CNF are heat-treated to temperatures up to 3000 °C. This high heat treatment creates the most graphitic carbon nanofibres and reduces the iron catalyst content to very low levels. Filler concentration for composites with CB was 2, 4, 6 and 8 vol.% and 4, 8, 12 and 16 vol.% for CNF.

2.2. Preparation and foaming of composites

Foaming of composites was carried out using the exothermic blowing agent Luvomax AZ-C1 (Lehmann & Voss & Co.), which consists of azodicarbonamide (ADC) and ethylene propylene rubber (EPM) carrier. Thermal decomposition of azodicarbonamide occurs at 200 °C resulting in the evolution of nitrogen, carbon monoxide, carbon dioxide, and ammonia gases. The chemical blowing agent was used in this study in an amount of 0.5 wt.%.

Polymer matrix and nanocomposites with a dimensions of 20 × 20 mm and a thickness of 3 mm were foamed by thermal decomposition of the ADC in a vacuum oven at 220 °C for 10 min.

2.3. Cellular structure characterization

Scanning electron microscopy (SEM) was used to characterize morphology of samples. Sputtering with gold was performed prior to SEM observations which were carried out with VEGA TESCAN microscope.

The foam density was evaluated by a buoyancy method with the density kit mounted on a balance from Mettler Toledo.

2.4. Thermal properties

The thermal analysis was performed using DSC Q20 from TA Instruments. All experiments were conducted at the heating rate of 10 °C/min, in the temperature range from 20 up to 220 °C. The samples of about 8 mg weight were placed in aluminum pans. After the first heating run, the samples were cooled down, and subsequently heated again with same rate. The glass transition temperature (T_g) and the melting temperature (T_m) were determined from the second heating run.

2.5. Volume resistivity measurements

In order to estimate precisely the percolation threshold of each polymer/filler system, electrical measurements of the volume resistivity as a function of the filler concentration were performed. Samples were prepared by press moulding in a form of plates and for minimizing the contact resistance, gold electrodes were vapour deposited on each sample. The current flow was measured using Keithley 6512 electrometer from Keithley Instruments, while the voltage supply was High Voltage Power Supply GPR-30H100 (GW Instek).

2.6. Electromagnetic shielding effectiveness

The measurements of real and imaginary part of electric permittivity were performed with HP 4282A (Agilent) Precision LCR Meter in the frequency range 100 Hz – 1 MHz. The apparatus was set in Cp-D mode, the sample capacity (in the absence of electrical field) was calculated on the geometrical basis. All measurements were performed in ambient conditions (room temperature: 24 °C, humidity level: 55%). Samples were produced in a form