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Investigation of contact surfaces between polymer matrix and metallic glasses in composite materials based on high-density polyethylene

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ABSTRACT

In our research we obtained composites based on high-density polyethylene (HDPE) reinforced with $Mg_{67.5}Ca_5Zn_{27.5}$ metallic glass by co-extrusion and compression. The co-extrusion and compression procedures have been provided at temperatures of supercooled liquid temperature region of both materials (between the glass transition temperatures (T_g) and crystallization temperature (T_x)). We investigated the mechanical properties and performed the structure characterization of the obtained polymeric/metallic glass composite samples. A positive effect of triethoxyvinylsilane on the adhesion between polymeric matrix and metallic glass reinforced particles was discovered. It was also found that composite samples (HDPE/$Mg_{67.5}Ca_5Zn_{27.5}$) had excellent adhesion, good thermal conductivity and high modules of elasticity. The metallic glassy samples demonstrated good dimensional stability after treatment by the 10 mass% of the triethoxyvinylsilane.

1. Introduction

At present, dual-phase and composite materials are widely used due to their good working properties. In particular, they provide a unique combination of strength and ductility. Application of reinforcing elements allows a significant improvement on the mechanical properties of the composites. These properties relate to the use of amorphous metal ribbons as reinforcing components in metals, concrete, and polymer matrices composites [1–9]. Some of the advantages of metallic glasses (depending on their composition) are their high strength and hardness, excellent corrosion and wear resistance, as well as unusual magnetic softness [10,11]. In addition, the near net shape casting of metallic glass is an inexpensive one-step process.

It is well known that metallic glasses have extremely high strength; however, they lack tensile plasticity, which restricts their potential applications [12]. On the other hand, polymer materials have high ductility and low density, though strength of these materials is rather low. Therefore, obtaining a new class of lightweight, ductility, and high-strength materials based on metallic glass and a polymer would solve the problem related to the improvement on the mechanical properties of structural materials. Such materials can be used as next-generation materials used in aircraft and automotive industries.

Currently, different titanium plates and screws for fixing bone fragments are widely used in surgery. Despite positive properties of such kind of fixation, there are many cases when titanium clips need removing after the consolidation of bone fragments. Plates and screws are made of bioresorbable materials can be an alternative to using titanium plates. The mechanical strength of these materials may be close to titanium and is sufficient to functionally stable fixation. These materials are considered promising and are widely used in the practice of foreign surgeons.

Materials consisting of metallic glass and a polymer have been produced earlier [13–16]. For example, Kundig A.A. et al. [17] obtained composites based on metallic glass and a polymer as a second soft phase. The authors argued that the joint processing of metallic glass and a polymer is possible. The authors also confirmed that the viscosity of some metallic glasses with a low glass transition temperature is close to the viscosity of a polymer at similar temperatures. In the same work, the authors revealed poor adhesion between a metallic glass and a polymer binder. The authors of the work [18] had a similar objective: to obtain composites with improved mechanical properties using microwave heating for the joint sintering. In their research they used thermoplastic polymers with a relatively low melting temperature and metallic glass with a glass transition temperature close to thermoplastic.

Thus, profound interest to metal/polymer composite materials may cause the development of dual-phase materials based on metallic glass (with a low glass transition temperature) and a polymer binder to improve constructional materials. Such materials can be obtained by co-extrusion or compression of powders of these materials at a temperature, within the supercooled liquid temperature region: i.e., between the glass transition temperatures (T_g) and crystallization

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temperature (T_x) — in case of metallic glasses and above T_g for polymeric materials. Extrusion or pressing on the supercooled liquid temperature region of both materials should allow interlacing these materials with each other and forming a two-phase material with high performance properties. In order to harden a polymer, it is necessary to use metallic glass with a relatively low T_g close to the polymer melting point [24], such as Ce— [19], Au— [20], Mg— [21], La— [22], and Pt— [23] based metallic glasses.

Mg-based metallic glasses are promising structural materials due to their sufficiently low weight and relatively good mechanical properties [25–28]. In this regard, metallic glasses based on Mg–Zn–Ca should be very useful for the preparation of polymer/metallic glass composites material. These glasses are considered to be excellent biomedical materials that can be used as biodegradable implants [29]. Also, materials based on magnesium alloys are widely used as structural components of bioresorbable materials for fixing bone fragments in surgery [30, 31]. The strength of such amorphous alloys, capable of exceeding 800 MPa stress and plastic strain, reaches 3.5% [32]. We consider creating a composite material using the metallic glass $Mg_{67,5}Ca_5Zn_{27,5}$ the high-density polyethylene (HDPE) really attractive because the HDPE has a suitable melting point in the supercooled liquid temperature region of the Mg based metallic glass. Also, it should be noted that in some cases HDPE is used for medicinal application [33,34,35].

In this regard, the aim of this work is to study a possibility of creating two-phase materials based on a polymer reinforced with metallic glass that have good adhesion between a matrix and a filler. In addition, this research study aims to analyze the mechanical properties (strength and ductility) of the materials obtained.

2. Material and methods

A metallic glass ribbon $Mg_{67,5}Ca_5Zn_{27,5}$ was used for the sample preparation. The ingots of Mg–Ca–Zn alloys were prepared by induction melting in argon atmosphere from the mixtures of pure metals Mg (99.9 mass% purity), Ca (99.9 mass% purity), and Zn (99.99 mass% purity). The ribbon samples were prepared by a single copper roller melt spinning technique. The thicknesses of the obtained ribbon were 0.02–0.03 mm and the wide 4.7–4.9 mm.

The structural and phase composition of the samples were examined by X-ray diffractometry with monochromatic CuK_α radiation. The microstructure of the samples was examined by scanning electron microscopy (SEM) carried out at 15 kV. The SEM micrographs were obtained in a secondary electron signal. The thin Pt coating (usually 10 nm) was sputtered on the composites surface for electrical conduction conditions.

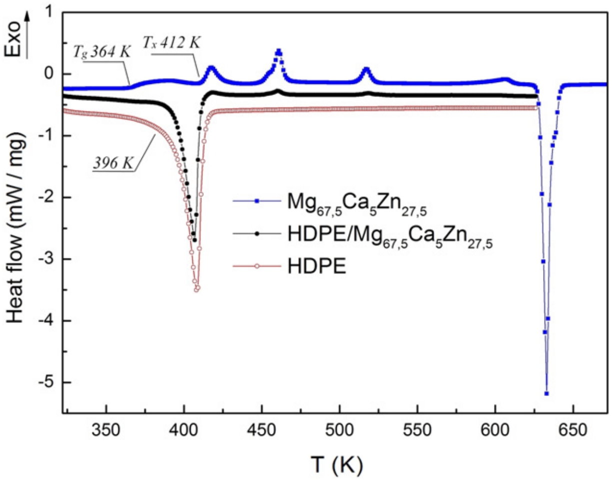

Fig. 2. DSC analyses of the: $Mg_{67,5}Ca_5Zn_{27,5}$ ribbon sample; high-density polyethylene powder sample and the obtained composite sample $HDPE/Mg_{67,5}Ca_5Zn_{27,5}$.

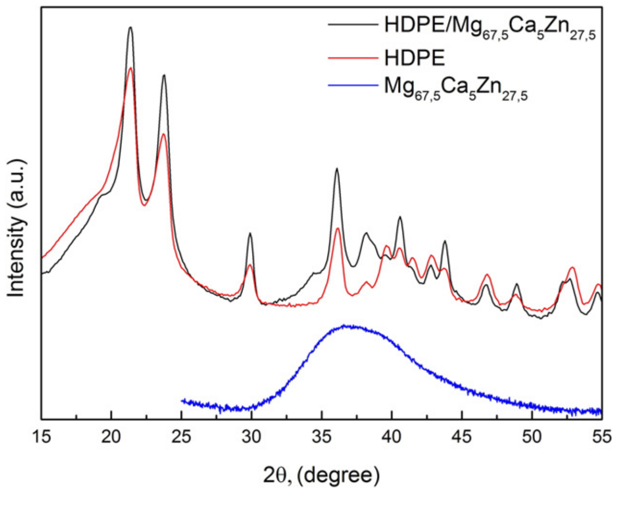

Fig. 1. XRD pattern of the: $Mg_{67.5}Ca_5Zn_{27.5}$ ribbon, high density polyethylene powder and the composite $HDPE/Mg_{67.5}Ca_5Zn_{27.5}$ sample.

In our research we used high-density polyethylene (HDPE) with the average particle size of about 200 μm as matrix composite samples.

The study of the thermal stability and the heat capacity of the prepared samples were provided by the differential scanning calorimetry (DSC) on the NETZSCH DSC 204 F1 Phoenix. The measured temperature ranges were from room temperature to 873 K and 383 K (for heat capacity) with the heating rate 10 K/min.

The Netzsch LFA 447 NanoFlash provided a thermal diffusivity analysis of the composite materials. The composites materials were investigated in the temperature range 297–373 K. The thermal conductivity was analyzed in accordance with the requirements of ASTM E1461.

The density of the obtained samples was measured by the hydrostatic weighing method using analytical balance AND GR-202, with using set for density determination AND AD-1653, in ethanol.

The tensile mechanical tests of the composites were carried out on a Zwick Z 020 universal testing machine at a speed of 10 mm/min at room temperature. For the tensile tests, the samples 85 mm in length, 10 mm in width, and 3.8 mm in thickness were used.

In order to improve the adhesion between the surfaces of the metallic glass and the polymer, we used triethoxyvinylsilane ($C_8H_{18}O_3Si$ —

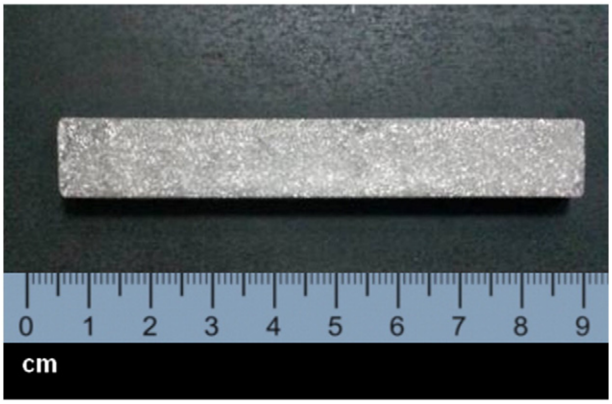

Fig. 3. The composite sample based on HDPE and the metallic glass ribbon ($Mg_{67,5}Ca_5Zn_{27,5}$).