Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Basaltic glass fibers with advanced mechanical properties

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ARTICLE INFO

Keywords:
Basalt fibers
Glass strength
Mechanical properties
Glass structure

ABSTRACT

In the present research the dependence of compositional variations on the basaltic glass fibers mechanical properties was explored. Addition of 15 mol % MgO or 5 mol % ZnO led to enhanced for tensile strength up to 43% and 47% and for modulus up to 13% and 25% respectively. The structure of basaltic glass fibers with varying MgO and ZnO contents was investigated by solid-state ^{29}Si and ^{27}Al nuclear magnetic resonance with magic angle spinning (MAS-NMR) and infrared (IR) spectroscopy. It was indicated that the increase of MgO and ZnO contents slightly decreased the degree of network polymerization. ^{27}Al MAS NMR exhibit a peak consistent with tetrahedral aluminum units AlO_4. The noticeable fraction peaks of narrow octahedral aluminum units AlO_6 are observed. Presence of aluminum cations in coordination 4 and 6 was confirmed by IR spectroscopy. In order to study their crystallization ability the glasses were heated at various temperatures for various time periods with following self-cooling. The crystalline phases were identified by X-ray diffraction analysis. Obtained results have shown the possibility to increase mechanical properties of continuous fibers and composites on their base by 50–60%.

1. Introduction

In recent years significant growth is observed in the manufacture of composite materials. Intensively developed reinforced plastics are used in different sectors of industry and technology. They successfully replace traditional construction materials and also can be applied to conditions that exclude the use of metals. Glass fibers are necessary components of different composite materials and reinforced plastics are the most important of them. Clearly for such applications, the development of high-strength and high-modulus glass fibers is of great importance. At the present time several works have been performed on development of modern continuous fibers from basalt stones [1,2]. Basalt is a natural material that is found in volcanic rocks originated from frozen lava, with a total melting temperature up to 1700 °C. Basalt (basaltic) glasses are complex aluminosilicate systems. Basalt continuous fiber (BCF) chemical composition varies widely. Their mechanical properties and production conditions are the function of the composition [3,4]. *E*-glass fibers are an aluminoboronsilicate glass fibers with an alkaline content of less than 2 wt% and have worse chemical resistance than basalt fibers [5,6].

Mechanical properties of glass fibers can be improved in various ways. For example, it is possible to use thermal tempering when a glass product is quenched at softening temperature [7] or the ion-exchange procedure [8]. The coating modification is another effective way to enhance the mechanical properties of basalt fibers and the properties of basalt fiber/epoxy resin composites [9].

It has been shown that the cations play a complex structural role in the oxide glasses, as they occur in different kinds of environments, which allow them to exert a contrasted influence on physicochemical properties of these glasses [10–12]. Many glass properties, such as coloration, chemical resistance, mechanical properties, crystalline nucleation and phase separation or ionic and electrical conductivity, may depend on glass structure. In turn, the structure is defined by the glass composition. In some cases it is possible to establish relations with the structural role of some key elements.

Thus, due to the compositional complexity it is not easy to give a simple structural picture of the basaltic glasses. We present in this research work some structural characteristics that appear to control physicochemical properties of multicomponent glasses, with a special attention to cations, which control the polymeric structure. The focus is placed on detecting the responses of structure and mechanical properties to systematic changes in chemical composition. We report a route to produce high-strength and high-modulus basaltic glass fibers for composites. It consists in modifying typical basaltic glasses compositions with 5–15 mol% MgO and ZnO.

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http://dx.doi.org/10.1016/j.jnoncrysol.2017.09.042
Received 15 June 2017; Received in revised form 12 August 2017; Accepted 20 September 2017

Table 1
Chemical composition in mol %, density (ρ) and glass transition temperature (T_g).

Specimen	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	ZnO	ρ (kg/m^3)	T_g (K)
BCF	63.6(6)	10.2(3)	0.9(1)	5.2(2)	12.0(3)	**4.7(2)**	1.2(1)	2.2(2)	–	2649(1)	680(2)
Mg5	60.6(6)	9.7(3)	0.9(1)	4.6(2)	11.5(3)	**9.5(2)**	1.1(1)	2.1(2)	–	2682(1)	681(2)
Mg10	57.4(6)	9.2(3)	0.8(1)	4.3(2)	10.8(3)	**14.3(2)**	1.1(1)	1.9(2)	–	2699(1)	679(2)
Mg15	54.3(6)	8.7(3)	0.8(1)	4.1(2)	10.2(3)	**19.1(2)**	1.0(1)	1.8(2)	–	2717(1)	678(2)
Zn5	60.5(6)	9.7(3)	0.9(1)	5.0(2)	11.4(3)	4.5(2)	1.1(1)	2.0(2)	**4.8(2)**	2692(1)	676(2)
Zn10	56.8(6)	9.3(3)	0.9(1)	4.8(2)	10.9(3)	4.3(2)	1.1(1)	2.0(2)	**10.1(2)**	2810(1)	674(2)
Zn15	53.3(6)	8.9(3)	0.8(1)	4.6(2)	10.4(3)	4.1(2)	1.0(1)	1.9(2)	**15.0(2)**	2903(1)	656(2)

2. Experimental procedure

2.1. Sample preparation

Producing basaltic glass fibers (BGF) with various MgO and ZnO contents was performed in two stages. In the first stage magnesium- and zinc-rich basalt bulk glasses were prepared by adding reagent grade chemicals MgO, ZnO to milled basalt batch (Sil'tsevskoe deposit, Carpathians, Ukraine). Each sample was heated in a Pt-Rh crucible at a rate of 250°/h to 1200 °C and at 50°/h in a range 1200–1600 °C and then held at 1600 °C for 24 h. The bulk glass was quenched from 1600 °C to room temperature by rapid pouring the melt into water.

The chemical compositions of the basaltic glasses with MgO and ZnO were analyzed by X-ray fluorescence analysis. The chemical compositions and specimen designation of fibers are presented in Table 1. Total iron content was restated as Fe_2O_3. The error of composition measurement was ± 1%.

In the next stage, BGF were produced using a laboratory scale system [3]. The accuracy of fiber manufacturing temperature measurement was ± 10° C. A control of fiber diameter was performed by varying the rotation rate of the reel. In this work fibers with 10–12 μm in diameter were used. Fibers were produced without sizing.

2.2. X-ray fluorescence analysis

X-ray fluorescence analysis of the specimens was performed on a PANanalytical Axios Advanced spectrometer. Characteristic X-rays were excited using a 4 kW Rh-anode X-ray tube. The excited radiation was recorded by a scanning channel with five exchangeable wave crystals and a detector. Measurements were performed in transmission geometry in vacuum. For measurements, it was used pellets of investigated glass with a binder.

2.3. XRD studies

X-ray diffraction (XRD) was made at room temperature on Thermo ARL X'TRA powder diffractometer ($CuK_{\alpha 1}$ radiation, λ = 1.54060 Å; $CuK_{\alpha 2}$ radiation, λ = 1.54443 Å). XRD patterns were collected in an angular range 2θ = 10°-60° at a scan step 2θ = 0.02° and a scan rate of 1° (2θ)/min. The phases were identified using the International Center for Diffraction Data (ICDD) database.

2.4. Thermal analysis

Differential scanning calorimetry (DSC) was performed on Netzsch STA Jupiter 449C equipped with a high-temperature furnace in a temperature range 20–1000 °C with heating rate 10°/min on high-sensitivity sample holder with Pt/Pt–Rh thermocouples. For measurement fibers have been grounded with an agate mortar and pestle. The procedure for measuring of T_g by DSC is described in details in [13].

2.5. Infrared spectroscopy

Pellets made of mixture of powdered glass and KBr in a weight ratio of 1:20, respectively, have been used for the measurements. FTIR spectra were measured using FTIR spectrometer Bruker Tensor 27. The absorption spectrum was recorded in the range 100–4000 cm^{-1}.

2.6. MAS NMR spectroscopy

The ^{27}Al and ^{29}Si MAS NMR experiments were performed on a Bruker AVANCE-II 400 spectrometer (field 9.4 T, ν^{27}Al = 104.3 MHz, ν^{29}Si = 79.5 MHz) using 4 mm double channel MAS probe with spinning rate of 12 kHz. The ^{27}Al MAS NMR spectra were recorded with π/12 pulse length of 0.6 μs, a recycle delay of 0.5 s and number of scans of 2048. The chemical shifts were referenced to $Al(NO_3)_3$. The ^{29}Si MAS NMR experiments were recorded with π/2 pulse length of 3.2 μs, a recycle delay of 2 s and number of scans of 1024. The chemical shifts were referenced to TMS ($Si(CH_3)_4$).

2.7. Density measurement

The hydrostatic weighing was used for the determination of glasses density at room temperature. A few fragments of each glass samples were weighed in air and water. The density values were determined using following equation:

$$\rho = \frac{W_a}{W_a - W_b} \cdot \rho_b \ \mathrm{kg}/\mathrm{m}^3 \quad (1)$$

where W_a is the weight of the sample in air, W_b is the weight of the sample in water, and ρ_b is the density of water. The density of water was 999.5 kg/m^3. Measurements were taken five times to obtain the most precise density values. The overall accuracy of these measurements was ± 0.5 kg/m^3 and the error in measurement was ± 0.05%.

2.8. Optical analysis

Optical analysis was made at magnifications of 200 × to 1000 × on an Olympus BX51TRF modular optical microscope (12V100WHAL lamp (Philips 7724) in transmission, U-LH75XEAPO xenon lamp in reflection) equipped with an Olympus C-5060 camera. ImageScope Color software was used for determination of the fiber diameter.

2.9. Mechanical properties

The tensile strength and Young's modulus were measured on a Hounsfield H100K-S universal tensile testing machine. Specimens were mounted in paper support frames using epoxy. The gauge length was 10 mm, and the crosshead speed was 5 mm/min (ISO 5079). At least 50 fibers have been tested to obtain the most accurate results. The error of tensile strength measurements were less than ± 5% and Young's modulus measurements were less than ± 4%.

3. Results

3.1. Mg- and Zn-rich basaltic glass fibers

It is indicated that the density (ρ) increases proportionally with