

EFFECT OF LOW-MELTING GLASS ON THERMAL AND PHYSICAL
PROPERTIES OF POLYMER COMPOSITESYaroslav Vakhula¹, Iryna Lutsyuk^{1, *}, Yuriy Melnyk¹, Olha Narok¹<https://doi.org/10.23939/chcht12.04.488>

Abstract. Low-melting glass has been synthesized in the system $\text{PbO-ZnO-B}_2\text{O}_3$ and $\text{Na}_2\text{O-P}_2\text{O}_5\text{-MoO}_3$ and its composition has been developed. The effect of the glass chemical composition on the softening temperature and the change of appearance during the heating have been established. Polypropylene-based composite with different content of glass powder as a filler was obtained. Thermo-physical properties of the composites were determined. Introduction of glass powder to the polypropylene composition damaged the material structure homogeneity. Using DTA method it was established that the developed filler shifts the temperature of polymer complete combustion toward higher temperature by above 40 K.

Keywords: low-melting glass, polypropylene, flame retardant, polymer composite.

1. Introduction

Glass is a unique material. A variety of technical and practical products are produced of glass. Moreover, in a softened state, glass forms protective surface coatings on metals (enamel) and ceramics (glaze). Powdered glass, both in pure form and as a component of a number of composite materials is widely used.

Most frequently glass powder is used in construction. By heat treatment of fine-grinded glass and gasifier mixture an effective porous heat-insulating material (foam glass) is obtained. Powder of soluble glass is used successfully for the production of hydraulic binder, which serves for the strengthening of soils, concrete, *etc.* [1]. The effective use of fine-grinded powder of bottle glass for the production of Portland cement is also well-known [2].

The glass powder of the $\text{PbO-ZnO-B}_2\text{O}_3\text{-SiO}_2$ system is used for glass-glass, glass-metal sealing, and double glazing [3]. Barabanov *et al.* [4] used glass powder of the $\text{NaPO}_3\text{-ZnB}_2\text{O}_4$ system with a mixture of coloring components for the preparation of decorative paints. In many cases low-melting glass is used for the manufacture of an abrasive tool based on electrocorundum [5].

Modern medicine uses glass powder with great success. Thus, on the basis of bioglass containing calcium and phosphorus ions, flexible implants, as well as fillers for eliminating bone defects are produced. Materials on the basis of bioglass found wide application in dentistry. In particular, L. Hinch [6] developed a bioactive glass powder for mouth sanitation. Due to its application, the sensitivity of the teeth decreases. Biopowder closes the root canals, leaving phosphorus and calcium ions on its surface. Glass powder is an irreplaceable component of ionomer cements, which are used in the therapy and teeth prosthetics [7]. The main component of the Sensodyne toothpaste is bioglass powder.

One of the most effective ways of glass powder application is its use as a filler for plastics. Being brought into the flame, the polymer materials begin to decompose. The starting temperature of destruction and the products that are released in this way determine the combustibility of the polymer. Flammability can be lowered by the introduction of special fillers – flame retardant [8, 9]. Glass as an inorganic flame retardant began to be studied recently. Such additives to polymers make them more resistant to combustion, while reducing the smoke formation.

Preferably, glass powder is used to reduce the combustibility of thermoplastics, namely, polyethylene, polypropylene, polyvinyl chloride, and polycarbonate. In this case, low-melting glass with the softening temperature of ≤ 673 K is used. It is thought that the creation of a polymer-glass composite provides safety when used in structural and building materials and for electrical equipment.

The high efficiency of flame retardants is based on the use of low-melting glass as a filler. When the polymer is burning, the glass is melting at high temperatures, covers the surface of the polymer and blocks the access of oxygen, making the combustion stop. It has been established that the use of glass as a flame retardant in polyvinyl chloride leads to the reduction in smoke generation by 90 % [10]. Moreover, after addition of glass powder, other operational properties of plastics, physico-mechanical, in particular, are expected to be improved.

Low-melting glass can be divided into groups by the name of the element or oxide, which is a part of the glass, and reduces the melting temperature. The most

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efficient glasses include phosphate, molybdenum, zinc, and borate ones.

The purpose of this work is to synthesize low-melting glass and to investigate its effect on the thermo-physical properties of polypropylene based composites.

2. Experimental

All materials used, namely PbO, ZnO, H₃BO₃, Na₂CO₃, Na₂HPO₄, Na₃MoO₃, were of high purity. The glass was cooked in an electric oven at 1223 K with isothermal holding for 1 h. A part of the melted mass was poured onto a steel plate and burned off; the rest was poured onto water and porous granulate was formed.

The gradient method was used to determine the temperature interval of the phase transformations of the resulting glass during heating. The boundaries of transformations temperature regions in the interval of 373–1073 K were determined visually.

Polypropylene powder (PP) purchased from Moplen HF501N (Basell, the Netherlands) with a density of 900 kg/m³, Vicat heat resistance of 428 K, and melt flow index $MFI_{230/2.16} = 18.5$ g/10 min was used to obtain polymer-silicate composites. The size of PP powder was less than 1 mm.

PP powder and low-melting glass were mixed in special glass containers with plastic corks, under constant stirring for 5 min. Composites based on the obtained polymer-silicate mixtures were melted in a chamber of a capillary extrusion plastometer for 5 min at the temperatures of 483 and 503 K, followed by extrusion through a capillary with the internal diameter of 2.095 mm and the length of 8.0 mm. The resulting strands were chopped with cutters.

The melt flow index of polymer composites (*MFI*) was determined using an extrusion plastometer "IIRT-M"

according to the standard method. A capillary with the internal diameter of 2.095 mm and the length of 8.0 mm was used.

The melting temperature of the polymeric composites was measured using a special metal plate equipped with a control thermometer, which was heated by an electric stove. The heating rate of the device was 2 K/min. The tack temperature and the temperature of the beginning of deformation under load (heat resistance) were fixed as well.

3. Results and Discussion

On the basis of the literature analysis it was concluded that compounds with molybdenum are effective flame retardants and suppressors of smoke formation. In addition, zinc-borate systems deserve attention.

In this connection, glass systems of PbO-ZnO-B₂O₃ and Na₂O-P₂O₅-MoO₃ have been selected for the researches. The glass compositions are shown in Table 1.

The visual analysis of the synthesized glass quality and its state after heat treatment allows to evaluate the resulting products (Table 2).

So, the P-1 glass is crystallized immediately at the time of pouring out and cannot be used. The glass P-2 has low values of softening temperature and viscosity already observed when poured out. At the temperatures above 693 K the glass is crystallized. It is obvious that its further crystallization can additionally increase the protective action of the polymer and the strength of the composite as a whole. The softening temperature of P-3 glass is considerably higher compared with the previous ones, but with increasing temperature it spreads and forms a homogeneous quality coating.

Table 1

The chemical composition of the synthesized glass systems

Glass symbols	Oxides content, wt %					
	PbO	ZnO	B ₂ O ₃	P ₂ O ₅	Na ₂ O	MoO ₃
P-1	85	10	5	–	–	–
P-2	75	15	10	–	–	–
P-3	70	20	10	–	–	–
M-1	–	–	–	15	15	70
M-2	–	–	–	25	15	60
M-3	–	–	–	35	15	50

Table 2

Quality and softening temperature of glass systems

Glass symbols	Color		Softening temperature <i>T_f</i> , K
	glass	coating	
P-1	golden-pink	yellow	crystallization
P-2	yellow-green	blue	573
P-3	yellow-green	golden	723
M-1	white	white	623
M-2	grey	black	553
M-3	dark brown	light brown	613

The increase of P_2O_5 content to 25 wt % in the system $Na_2O-P_2O_5-MoO_3$ (glass M-2) decreases the softening temperature to 553 K. It should be noted that phosphate glass is a low-melting glass due to the presence of structure consisting of $[PO_4]$ -tetrahedrons. The ability of phosphates to form glasses depends on $R = A_2O+AO/P_2O_5$ ratio. This ratio defines the type of anionic matrix. In our case $R = 1$ (for M-1 glass), 0.6 (M-2) and 0.43 (M-3). The decrease in R value corresponds to the greater amount of ultraphosphate compound and leads to the increase of structure relatedness and thereafter, the improvement of glass properties. So, we can assert that the value of R for M-2 glass is the optimum and T_f value is the lowest.

Powders P-2 and M-2 were chosen to be used as a filler of polymer composite materials based on polypropylene. The composites with different kinds of filler of various concentrations are represented in Table 3.

MFI of different composites significantly differ. The introduction of M-2 powder in the quantity of 5 % increases the flow rate from 11 to 22.4 g/10 min. However, further increase in the content of glass powder up to 40 % reduces this value to 7.3 g/10 min. A similar picture is observed in the case of using P-3 powder. The obtained results make it possible to assert that composites No. 4, 5 and 8 can be formed not only by extrusion, but also by injection molding, which is important from a technological standpoint.

The focus was on the heat resistance and melting temperature. Even insignificant amount of lead-containing glass powder (glass P-3) increases the heat resistance by 8 K and the melting temperature by 5 K. Further increase in the glass content up to 40 % increases these values by 24 and 28 K, respectively. The introduction of various amounts of M-2 glass does not significantly affect the properties of the resulting products.

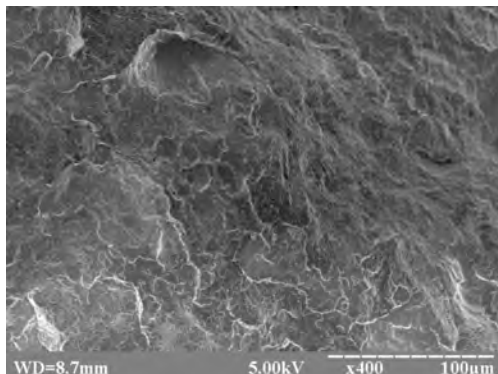
The above data convincingly point to the change in properties as a result of filling the polymer with a fine powder of inorganic low-melting glass. During heating, the polymer particles are cemented by glass due to its low softening temperature, thereby influencing the thermal and physical properties of the resulting material. At the same time, it can be noted that the synthesized glass powders as a filler increase the operating temperature of products by 30 K.

To determine the composites structure at the extrusion temperature we carried out electronic-microscopic studies. One can see from Fig. 1 that the structure of freshly fractured surface of a pure PP is homogeneous, without pores and defects. When we add M-2 powder in the amount of 40 %, the structure of the composite is changed considerably and becomes heterogeneous. There are pores and individual particles of glass powder with the boundary between them.

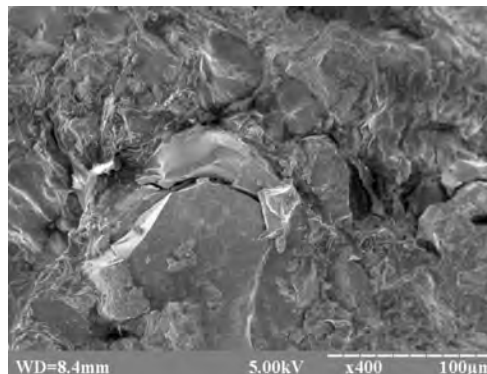
Table 3

Thermal and physical properties of the polypropylene-based composites and low-melting glass

Composite No.	Composition, wt %		MFI, g/10 min	Temperature, K		
	PP	filler		tack temperature	heat resistance	melting temperature
1	100	–	18.5	432	436	441
2	95	5 (M-2)	22.4	429	435	442
3	90	10 (M-2)	21.6	426	434	443
4	80	20 (M-2)	13.2	433	441	447
5	60	40 (M-2)	7.3	433	439	445
6	95	5 (P-2)	28.5	431	435	442
7	90	10 (P-2)	22.5	425	432	440
8	60	40 (P-2)	12.8	431	443	449



a)



b)

Fig. 1. The structure of samples fracture: pure PP (a) and composite No. 5 (b)

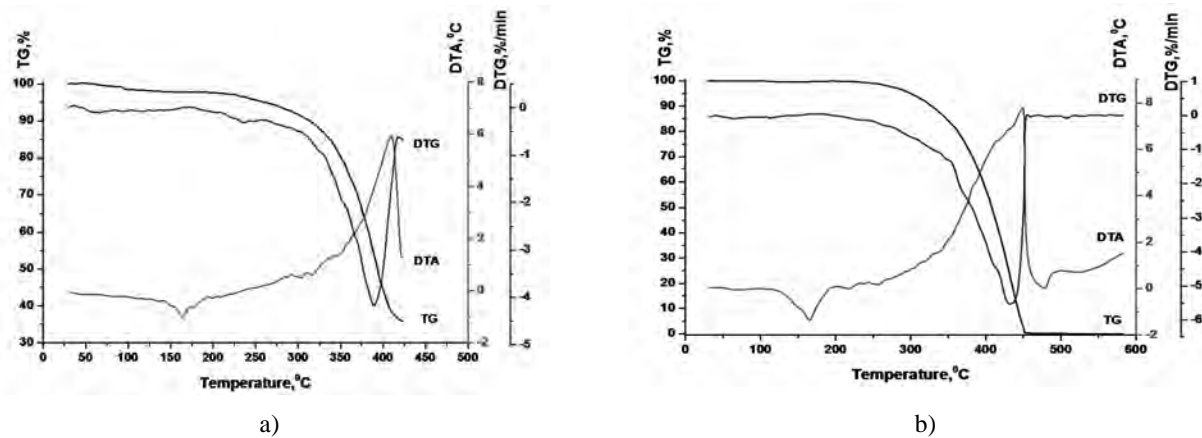


Fig. 2. Derivatograms of the samples: pure PP (a) and composite No. 5 (b)

The behavior of the samples during heating was studied by differential-thermal analysis (DTA). The presence of heat effects and mass change during heating are shown in Fig. 2.

For pure PP we observe the endoeffect with the maximum at 438 K caused by the polymer melting. During further heating there is a clear and rapid exoeffect at 683 K, which is accompanied by a significant loss in mass (TG curve) and associated with complete burnout of the sample. It should be noted that the mass reduction begins at 333 K. The DTA results of the composite No. 5 are significantly different. The endoeffect at 438 K is similar to the previous one. The loss in mass associated with combustion begins only at 503 K, which is by 170 K higher than for pure PP. The nature and maximum of the exoeffect are also significantly different. The maximum on the DTA curve corresponds to 723 K, and the total exoeffect (its area) is much larger, which gives grounds for asserting a much slower process of combustion and its proceeding at a higher temperature.

4. Conclusions

The glass systems of $PbO-ZnO-B_2O_3$ and $Na_2O-P_2O_5-MoO_3$ are characterized by low softening temperature. Molybdenum glass is more effective retardant for the polymer composite due to its low viscosity and narrow temperature region of crystallization. The introduction of low-melting glass powder into polypropylene creates a heterogeneous structure. The temperature of the complete combustion of the composite increases by 40 K, compared with polypropylene.

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ВПЛИВ ЛЕГКОТОПКОГО СКЛА НА ТЕПЛОФІЗИЧНІ ВЛАСТИВОСТІ КОМПОЗИЦІЙНИХ ПОЛІМЕРНИХ МАТЕРІАЛІВ

Анотація. Розроблено склади і синтезовано легкотопке скло в системі $PbO-ZnO-B_2O_3$ та $Na_2O-P_2O_5-MoO_3$. Встановлено вплив хімічного складу скла на температуру розм'якшення і зміну зовнішнього вигляду під час нагрівання. Одержано полімерний композиційний матеріал на основі поліпропілену з різним вмістом наповнювача – порошку скла. Визначено теплофізичні властивості композитів. Введення до складу поліпропілену порошку скла призводить до порушення однорідності структури матеріалу. Методом ДТА встановлено, що використання розробленого наповнювача змінює температуру повного згорання полімеру в сторону вищої температури майже на 40 °.

Ключові слова: легкотопке скло, поліпропілен, антипірен, композиційний полімерний матеріал.