1. Introduction

Nowadays polymeric materials are widely spread in almost all spheres of modern science and industry. One of the most important directions of the use of polymers and various compositions on their basis is to obtain transparent materials with luminescent properties. These materials have found broad application both in everyday life and in high-tech industries.

They are used for producing light-sensitive showcases and signs, detectors of various types of energy, optical fiber parts of machines and mechanisms, and the like. Polymers such as polystyrene (PS) and its derivatives, polymethylmethacrylate (PMMA) and their copolymers are widely...
used. Photosensitive (light sensitivity) materials on the basis of vinylcarbazole, polyorganosiloxanes, epoxies, vinylbiphenyl, vinylnaphthalene are also known, but they have not found application because of their poor solubility, low transparency and low light yield.

Synthesis and processing of these polymers into the finished optically transparent products is quite a difficult task from the point of view of the technological features of these processes. At the same time, a promising direction is the creation of these materials based on polycondensation polymers, in obtaining which it is much easier to regulate the molecular weight, spatial structure, composition. In addition, in comparison with polymerization material, polycondensation polymers have higher heat resistance and longer life. That is why this study is on the synthesis of new thermosetting highly transparent benzoguanamineformaldehyde polymers is of high relevance.

2. Analysis of literature data and problem statement

To date, there has been much research aimed at finding new transparent polymer bases, to obtain light-sensitive materials based on thermosetting polymers, which are characterized by higher operational characteristics than traditional thermoplastic optically transparent materials. The works of Japanese scientists describe the latest optically transparent materials based on polyolefins with a significant light energy transfer efficiency [1]. The work [2] is devoted to the development of new heat-resistant thermosetting acrylates of the heat-polymer type with the transparency of about 85% and the luminescence ability. The work [3] describes anti-corrosion hybrid acrylic-silicone oligomers of the thermosetting type with the ability to transmit light in the coating. The paper [4] deals with the development of highly transparent polyimide polymers with heat resistance over 200 °C and significant luminescence ability. The paper [5] gives the results of investigations of the optical characteristics and properties of highly transparent polymer materials for optoelectronics and photonics based on polyaniline, polyvinylcarbazole and polyphenylenevinylene. The paper [6] describes the optical materials on the basis of polydimethylsiloxane, which are characterized by a high level of heat resistance and long-term stability of operational characteristics. The publication [7] reveals information about the development of optically transparent polymers based on polyacrylic acid and polyethylene oxide to obtain heat-resistant transparent fluorescent films. The paper [8] presents the study on obtaining detectors and sensors based on transparent polymers of methyl methacrylate and vinyl acrylate with improved spectral characteristics. A wide range of new advanced optical thermosetting polymers is considered in the paper [9], which adequately describes their use in obtaining fiber-optic products. However, the technological complexity of obtaining highly transparent thermosetting polymers remains a big problem, as noted in the monograph [10]. According to the monograph [11], the synthesis and further processing of reactive polymers are associated with significant internal stress and chemical shrinkage, which almost always lead to instability of the optical characteristics during operation. At the same time, in [12] it is noted that the filling of the channels and forms in the processing of thermosetting oligomers has considerable specificity and often does not allow obtaining optically transparent products from these materials. No less significant challenges are associated with surface defects of products made of thermosetting oligomers in obtaining transparent parts [13]. Therefore, today obtaining highly transparent polymers of the thermosetting type is quite a challenge. The paper [14], presents the results of the successful synthesis of melamine-formaldehyde oligomers with high optical characteristics using modification by the proton-acceptor substances. According to the paper [15], these materials due to their optical-spectral characteristics are a promising basis for the fabrication of plastic scintillators. However, a moderate level of the quantum yield of luminescence – 6–7% is observed in these materials with a high transparency value (about 95%). That is why today benzoguanamineformaldehyde (BF) oligomers – colorless transparent materials, which in their structure have the ability to luminescence are of considerable interest from the point of view of obtaining transparent polymeric materials with luminescent properties. However, in scientific periodicals there is no data on the synthesis of optically transparent BF polymers.

3. The purpose and objectives of the study

The purpose of the study is the synthesis of optically transparent BF oligomers and polymers with luminescence properties and high operational characteristics.

To achieve this goal, you must perform the following tasks:

- to develop and explore the methods of synthesis of transparent BF oligomers and polymers;
- to investigate the spectral-luminescent characteristics of transparent BF oligomers.

4. Synthesis of highly transparent benzoguanamineformaldehyde polymers, studies of the physical, operational and optical-spectral characteristics of the synthesized polymers

The process of obtaining the transparent BF polymer consisted of the following stages.

1. The condensation of benzoguanamine with formaldehyde. The 250 ml three-neck flask, equipped with an anchor stirrer with a speed of rotation of 48 rpm, reflux condenser (partial condenser), thermometer, and water bath, was charged with formalin. Benzoguanamine was loaded in the formalin solution, neutralized to pH 3.8–4 when the operating stirrer and the reaction mixture was gradually heated to 60–70 °C. Stirring was conducted until complete dissolution of benzoguanamine in formalin. After complete dissolution of benzoguanamine, the reaction mixture was sampled for the analysis to determine the coefficient of refraction and pH, which were required to have the values equal to 1.410±0.002 and 8.0–9.5 respectively. Then, the solution was heated to the boiling point of the reaction mixture (94–98 °C) and let to stand (to withstand) thus for about 45 minutes. In the process of condensation, the pH of the solution was maintained at the level of 7.5–9.0.

2. Dehydration of the obtained BF oligomer: after receiving a positive result of the analysis on the completeness of the polycondensation reaction, the reaction mass was brought to
pH 7.5–8.5, cooling it to 75–85 °C. Dehydration of the BF oligomer was performed by vacuum distillation at a temperature of 75–85 °C.

3. Structuring of the dehydrated BF oligomer carried out in a glass form at 100–110 °C for 4–12 hours.

4. The modification was carried out by adding glycerol to BF oligomers at the time of completion of the polycondensation of formaldehyde benzguanamine, bringing the pH of the reaction mixture to 7.5–9.0 and withstanding it at 100 °C for 30 minutes with constant stirring.

Determination of molecular weight was carried out according to the Rast’s method, which is based on the ability of a solute to lowering the melting point or the freezing point of the solvent. Determination of the content of free formaldehyde and the methylol groups was performed by the method of chemical titration. Determination of dry residue was performed by the method according to GOST 14231. Determination of the relative viscosity of the oligomer was carried out at a temperature of 20.0 ± 0.5 °C on viscosimeter VZ – 4 with the nozzle diameter of 4 mm.

To determine the degree of cross-linking, the Soxhlet apparatus was used, which allows extracting the chemically unbound part of the oligomer by the boiling solution. The impact strength of the samples according to GOST 4647 and transverse rupture stress according to GOST 9550-81 for specimens without notch were determined on the impact pendulum-type testing machine 2083KM – 0.4. Determination of the relative viscosity of the oligomer was determined by hydrostatic weighing at 293 K according to GOST 15139.

Before the determination of operational characteristics, the samples were dried in an oven for 1 hour at a temperature of 378 ± 3 K. After drying, they were cooled in an exicator over calcium chloride and weighed each to the nearest 0.001 g. Determination of water absorption in cold water was conducted according to GOST 4650-80. Heat treatment of the samples was performed in the dry-air electrical cabinet «В-131» for 24 hours and a temperature of 373 ± 3 K. Then, slow cooling of the samples in the exicator over calcium chloride was performed.

The refractive index was determined using the refractometer IRF 454 according to standard methods. Electronic absorption spectra in the range of 200–500 nm were taken using the spectrophotometer U3210 «Hitachi» (Japan). The 50 W deuterium lamp was a light source. Luminescence spectra in the range of 250–700 nm were taken using the fluorescence spectrophotometers F4010 «Hitachi» (Japan) and FluoroMax-4 (France). The 50 W xenon lamp was used as a light source. The bulk attenuation length (BAL) was determined according to GOST 17038.3 by passing the helium-cadmium laser light with a wavelength of λ max=441 nm through the sample of the material of a certain length l and subsequent registration of the radiation intensity I transmitted through the sample by the photodetector.

5. Experimental data and discussion

The processes of synthesis of BF oligomers at various molar ratios of monomers were studied. It was found that the most effective formaldehyde (F) addition to benzguanamine (B) occurs at a molar ratio of B:F 1:1 (Fig. 1).

By increasing the molar ratio of B:F, the free F content in the reaction medium increases during the whole polycondensation process and in the resulting BF oligomers accounts for, wt %: 1:1–2.5, 1:2–3.2, 1:4–3.8.

Also, for the study of the polycondensation process and clarification of its basic laws, the studies on the determination of the rheological and molecular-weight characteristics of polycondensation solutions at different molar ratios of B:F were conducted.

Research of the relative viscosity (η) has shown that the gradual increase of it on average by 2 seconds in the first 40 minutes of the polycondensation is observed in all studied solutions (Fig. 2), and then a sharp jump (leap) of the relative viscosity by 4 seconds occurs in the last 10 minutes of the process.
condensation process has the same pattern as that for the relative viscosity (Fig. 3). The comparative analysis of Fig. 2, 3 shows that the jump in the relative viscosity in the last 10 minutes of the polycondensation process corresponds to an abrupt increase in the molecular weight of the BF oligomers.

Fig. 3. The change in the molecular weight in the polycondensation process at different molar ratios of B:F: 1 – 1:1; 2 – 1:2; 3 – 1:4

Thus, based on the results of the study of the polycondensation process of B and F at different molar ratio of B:F, it was found that the most effective addition of F to B occurs at a ratio of 1:1 resulting in the final product of polycondensation is the BF oligomer with a molecular weight of 260 g/mol and relative viscosity of 20 sec. While increasing the molar ratio of B:F, a decrease in the molecular weight and relative viscosity of BF oligomers is observed.

Table 1 presents the main characteristics of BF oligomers obtained by the polycondensation of B and F at different molar ratios. It shows that all obtained BF oligomers have a transmittance value at the level of 88–93 % and a refractive index 1.465–1.469, which allowed, on the one hand, calling them materials with high light transmittance and low refractive index and, on the other hand, using in further studies on the development of optically transparent BF polymers.

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>B:F 1:1</th>
<th>B:F 1:2</th>
<th>B:F 1:4</th>
</tr>
</thead>
<tbody>
<tr>
<td>χ, wt %</td>
<td>2.5</td>
<td>3.2</td>
<td>3.8</td>
</tr>
<tr>
<td>ζ, %</td>
<td>17.9</td>
<td>15.4</td>
<td>14</td>
</tr>
<tr>
<td>MW, g/mol</td>
<td>260</td>
<td>255</td>
<td>244</td>
</tr>
<tr>
<td>ζ, sec</td>
<td>19</td>
<td>18</td>
<td>15</td>
</tr>
<tr>
<td>T, %</td>
<td>88</td>
<td>91</td>
<td>92</td>
</tr>
<tr>
<td>n₀</td>
<td>1,469</td>
<td>1,466</td>
<td>1,465</td>
</tr>
<tr>
<td>Appearance</td>
<td>Colorless slightly gnarled (knag/knot) solution</td>
<td>Colorless transparent solutions</td>
<td></td>
</tr>
</tbody>
</table>

Note: * – χ is the free formaldehyde content, ζ is the methylol group content, MW is the molecular weight, ζ is the relative viscosity, T is the transmittance, n₀ is the refractive index

It is known that the most serious problem for the BF polymers are significant temporary and residual stresses due to the influence of the field of mechanical forces, nonuniform temperature and power deformations that accompany the struc-

turing of BF polymers. These stresses are also caused by the allocation of low molecular weight products when structuring and a considerable shrinkage, particularly chemical, which depends on the degree (fullness) of the structuring. Shrinkage also depends on the duration of the temperature and mechanical impact, and other factors that affect the course of the relaxation processes both in the bulk and on the surface of products. The occurrence of defects under the influence of temporary and residual stresses leads to a deterioration of the physical-mechanical and operational characteristics of finished products, including optical transparency.

Based on the above, the main purpose of the study of the structuring process was to determine the conditions, which would reduce the level of temporary and residual stresses that would provide highly transparent BF polymers with high physical-mechanical and operational characteristics. Table 2 presents the main physical and physical-mechanical parameters of BF polymers, structured at different temperatures and molar ratios of B:F.

Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low-temperature</th>
<th>Medium-temperature</th>
<th>High-temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρ, g/cm³</td>
<td>1.395</td>
<td>1.41</td>
<td>1.42</td>
</tr>
<tr>
<td>Shrinkage, %</td>
<td>1.4–1.6</td>
<td>2.0</td>
<td>2.1–2.3</td>
</tr>
<tr>
<td>w, %</td>
<td>1.5–1.7</td>
<td>0.7–0.8</td>
<td>0.6–0.7</td>
</tr>
<tr>
<td>n₀</td>
<td>63.5</td>
<td>61.4</td>
<td>60.2</td>
</tr>
<tr>
<td>T, %</td>
<td>43–45</td>
<td>46–48</td>
<td>50–51</td>
</tr>
</tbody>
</table>

Note: * – ρ is the specific density, w is the water absorption, n₀ is the transverse rupture stress, a is the impact strength

Table 2 shows that none of the studied conditions provide highly transparent BF polymers with time-stable physical and mechanical characteristics. The low-temperature conditions are characterized by turbidity and severe cracking of the samples of BF oligomers upon cooling and demolding, and high-temperature – their strong foaming, cracking and coloring.

Turbidity, a significant allocation of low-molecular weight products on the surface and high water absorption, which is due to the low completeness of the cross-linking process and the presence of defects are also characteristic of the low-temperature structured samples.

The medium-temperature conditions at 110–120 K was noted as optimum, in which the negative phenomena, typical for low and high-temperature conditions are not observed, but they are marked by a gradual cracking of the BF polymer in a relatively short period of time (up to 12 hours) after demolding.
The most appropriate molar ratio of B:F is 1:2 ratio, which, while ensuring a sufficiently high degree of cross-linking allows avoiding turbidity and strong gnarl (knot, twist), which are characteristic of the BF polymers with a ratio of B:F 1:2.

Thus, the studies of all the stages of the synthesis of BF polymers allowed determining the optimal molar ratio of B:F and eliminating a number of factors that adversely affect the transparency (yellowing, separation of low-molecular weight products of the samples, shrinkage, etc.).

In addition, it was found that it is impossible to obtain materials with high and stable in time optical properties because of significant temporary and residual stresses in the structured BF polymers. The high level of temporary and residual stresses leads to micro-cracks, expansion and warping of the finished products. Therefore, further studies were focused on the modification of BF oligomers, which would reduce the level of temporary and residual stresses, and consequently, provide the material with high optical characteristics.

Table 3 presents the main technological, physical and physical-mechanical properties of materials obtained at different contents of glycerol.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\rho$, g/cm$^3$</th>
<th>Shrinkage, %</th>
<th>$\varepsilon$, %</th>
<th>$\sigma$, MPa</th>
<th>$\gamma$, %</th>
<th>$\delta$, %</th>
<th>$\tau$, %</th>
<th>$\eta$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original BF polymer</td>
<td>1.4</td>
<td>1.2</td>
<td>0.7</td>
<td>0.3</td>
<td>65</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glycerol-modified 10 wt %</td>
<td>1.40</td>
<td>0.25</td>
<td>0.35</td>
<td>45</td>
<td>3.1</td>
<td>65</td>
<td>80</td>
<td>1.55–1.58</td>
</tr>
<tr>
<td>Glycerol-modified 20 wt %</td>
<td>1.422</td>
<td>0.15</td>
<td>0.25</td>
<td>60</td>
<td>6.68</td>
<td>63</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>Glycerol-modified 40 wt %</td>
<td>1.48</td>
<td>0.12</td>
<td>0.17</td>
<td>330</td>
<td>3.6</td>
<td>60</td>
<td>93</td>
<td></td>
</tr>
</tbody>
</table>

In the analysis of experimental data on modification of BF polymers, it was found that the modification of BF oligomers with the glycerol content of 20 wt % provides materials with high light transmittance, low residual stress, shrinkage and water absorption and high physical-mechanical characteristics. At the same time, such an important characteristic of scintillation plastics as BAL in the above-mentioned materials is at the level of PS and PMMA – 40–60 cm to 50–200 cm.

The spectral-luminescent properties of BF oligomers and polymers with different molar ratio of B and F were investigated. With increasing B content, the maximum absorption band is shifted towards higher wavelengths, and its intensity increases (Fig. 4).

Changes in the absorption spectra of BF polymers have a different nature: with increasing B content, the band at 280–290 nm becomes more intense, and the intensity of the band at 315–325 nm significantly increases (Fig. 5).

A similar pattern is observed in the study of luminescence excitation spectra: the increase in the overall level of the excitation peaks and an increase in the intensity of the band at 315–325 nm significantly increases (Fig. 6). A similar pattern is observed in the study of luminescence excitation spectra: the increase in the overall level of the excitation peaks and an increase in the intensity of the band at 315–325 nm significantly increases (Fig. 6) with increasing molar ratio of B:F: 1 – 1; 2 – 2; 3 – 4.

The study of the luminescence spectra of BF polymers with different molar ratios of B:F (Fig. 7, 8) showed that with increasing molar ratios, there is an increase in the overall level of the luminescence intensity of the BF polymers at the light-excited luminescence with $\lambda_{ext}$=270 nm, and with $\lambda_{ext}$=320 nm.
Технологии органических и неорганических веществ

74 Fig. 8. Luminescence spectra of (\(\lambda_{\text{ext}}=320\) nm) of BF polymers with different molar ratios of B:F: 1 – 1; 2 – 2; 3 – 4

Also, the luminescence peak shift towards larger wavelengths under the light-excited luminescence with \(\lambda_{\text{ext}}=270\) nm is typical, whereas under the light-excited luminescence with \(\lambda_{\text{ext}}=320\) nm, the hypsochromic effect is observed.

Table 3, which presents the main spectral–luminescent characteristics of BF oligomers and polymers shows that with increasing molar ratio, the extinction coefficient and the relative quantum yield of luminescence increase, while the luminescence time of BF polymers remains at the level of 1–2 nsec.

So, BF oligomers and polymers are characterized by the intense luminescence in the wavelength range of 260–265 nm, which increases with an increasing molar ratio of B to F, the extinction coefficient and the quantum yield of luminescence of oligomers and polymers also increase.

6. Conclusions

1. The study of the synthesis of transparent BF oligomers and polymers with luminescent properties was carried out. The physical-chemical regularities of the process of producing transparent BF oligomers and polymers with spectral-luminescent properties were investigated. It is shown that the modification of BF oligomers with glyceral with a content of 20 wt. % allows obtaining materials with high light transmittance (90–91 %), low residual stress (10–20 MPa) and shrinkage (0,15 %).

2. BF polymers, which are characterized by low water absorption, high physical–mechanical characteristics when the light transmittance of about 90 % were synthesized. It was found that such an important characteristic of scintillation plastics BAL, in the above-mentioned materials is at the level of PS and PMMA – 40–60 cm to 50–200 cm.

3. The main spectral–luminescent characteristics of transparent BF oligomers and polymers were investigated. It is shown that they are characterized by the extinction coefficient of up to 9000–12000 and the intensity of the luminescence with the relative quantum yield of up to 10 % in the range of 360–365 nm.

References

INVESTIGATION OF SPECTRAL CHARACTERISTICS OF CHOLESTERIC LIQUID CRYSTALS AT CARBOHYDRATES INFLUENCE

M. Vistak
Candidate of Physics and Mathematical Science, Associate Professor*  
E-mail: vistak_maria@ukr.net

V. Dmytrak
Teacher*  
E-mail: dmywas@gmail.com

J. Horbenko
Junior Researcher
Department of Physical and Colloid Chemistry  
Ivan Franko National University of Lviv  
Kyrylo and Melodya str., 8, Lviv, Ukraine, 79005  
E-mail: y_bilka@ukr.net

O. Sushynskyi
Doctor of technical science, Associate Professor  
Department of electronic devices  
Lviv Polytechnic National University  
Bandery str., 13, Lviv, Ukraine, 79013  
E-mail: orest.y.sushynskyi@pnu.ua

*Department of Biophysics  
Danylo Halytsky Lviv National Medical University  
Pekarska str., 69, Lviv, Ukraine, 79010

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1. Introduction

Determination of the concentration of the most common carbohydrates in the human body, food, pharmaceutical forms is a topical issue in medicine for diagnosing pathologies, and in the diet therapy for determining the carbohydrate concentration in food. Optical sensor systems in which detection of carbohydrates is based on the change in the spectral characteristics of the sensitive medium are the most promising. However, the vast majority of such optical systems have a number of unresolved problems caused by a difficulty of registration of the selected optical effect, or a complex multi-layered structure of the sensing element. This complicates their application mainly because of the high cost.

We suggest using a cholesteric liquid crystal with the reflection band, which lies in the visible spectrum as the sensing element of optical carbohydrate sensors.