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SYNTHESIS AND PROPERTIES OF OPTICALLY TRANSPARENT COMPOSITE ON THE BASIS OF BUTYL METHACRYLATE COPOLYMER WITH STYRENE

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Abstract. For creation of optically transparent material with complex properties it has been synthesized the copolymer of butyl methacrylate with styrene at various molar ratios of comonomers. The physical-mechanical characteristics of the synthesized copolymer have been investigated. It has been established that by copolymerization of butyl methacrylate with styrene one can obtain the optically transparent material with the best physical-mechanical properties. It has been revealed that the synthesized copolymer possess high optical transparency (n_D^{20} =1.5870). The dependence of spectral transmission coefficient of butyl methacrylate with styrene on composition and microstructure of copolymer has been studied. The obtained copolymer has been modified by nanoparticles of $Cu(CH_3COO)_2$. The dependence of spectral coefficient of the synthesized composites on content of components has been investigated. The copolymer obtained on the basis of monomers of BMA+St, modified by nanoparticles of $Cu(CH_3COO)_2$ show higher optical transparency(n_D^{20} =1,5940) than the copolymer of butyl methacrylate with styrene (1.5870). A light transmission of the obtained composite (90%) is higher than in the copolymer BMA+St (88%).

Keywords: *butyl methacrylate, styrene, copolymerization, optically transparent materials, nanocomposite, light transmission.*

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1. Introduction

New tendencies of the development of optically transparent materials and technologies lead to the creation of optically transparent nanocomposites. It is generally accepted that socially-economic progress in the 21st century will be entirely determined by the success of nanotechnology. At the nanometer scale, qualitatively new effects, properties and processes determined by quantum mechanics, dimensional quantization in small structures and other phenomena and factors arise (Pool, 2006; Gusev, 2005). The polymer-metal nanocomposites as the composition materials possessing whole complex of unique properties are of particular interest. This makes the polymer-metal nanocomposites very attractive as the functional optical materials. Polycarbonates, polymethylmethacrylates, polystyrene and their derivatives play an important role for creation of the functional optically transparent compositions. The exceptional optical properties of PMMA (light transmission of 92%) and the possibility of various modifications provide wide application of this material in light-engineering, optics, etc. One of the defects of PMMA is thermal instability and low adhesion capacity (Krul *et al.*, 2008). For elimination of these defects and improvement of physical-mechanical properties, the styrene and its derivatives are often used in MMA copolymerization reaction. By varying the ratio of the initial components and the conditions of carrying out of process of the polymer composition materials there are obtained the polymer materials with the required properties (Xu *et al.,* 1988; Smagin *et al.,* 1991; Sveshnikova & Kazannnikova, 1994; Smagin *et al.*, 1999; Burunkova *et al.*, 2008).

At the same time, nanometals are of particular interest among the numerous polymer modifiers. They are implemented into polymer matrices with dissolution of the metal compounds in monomers or in complex polymerized mixtures, and also with the exchange interaction of the metal-containing compounds with macromolecules containing reactive groups or with (co)polymerization of the metal-containing monomers.

In this connection, the purpose of this work was the preparation of optically transparent nanocomposites differing with high light transmission and the best physical-mechanical properties. The object of the investigation was the copolymerization reaction of butyl methacrylate (BMA) with styrene (St), and the obtained copolymer has been modified with nanoparticles of $Cu(CH_3COO)_2Cu(CH_3COO)_2$.

2. Experimental

The copolymerization reaction of BMA with St was carried out in ampoules in a benzene solution in the presence of 0,2mol % of AIBN from total quantity of comonomers at 70°C. The forming copolymers were purified by twofold precipitation from benzene solutions with methanol and dried at 30°C in a vacuum (15-20 mm merc.c.). The total concentration of the initial monomers was constant and was 2.0 mol/l, and the molar ratio of the initial monomers was varied in the ranges shown in Table 1, by addition of the reaction mixture to pentane excess. After the specified time (10-20 min), the copolymers with various compositions of comonomer were isolated. The conversion of the copolymer samples, for which the copolymerization constants were calculated, was 8-10%.

The composition of copolymer has been calculated on the basis of data of elemental (Braun *et al.*, 2016) and IR spectral analyses.

The IR spectra of the initial monomers and synthesized copolymer were recorded on a spectrometer “Agilent Cary 630 FTIR” of firm “Agilent Technologies”, and the PMR spectra – on a spectrometer “Fourier” of firm “Bruker” (FRG) (300.18 MHz) in a dioxane solution.

The copolymer is a powder of white color, well soluble in benzene, chloroform and carbon tetrachloride.

The parameters of microstructure of the copolymer have been determined by means of equation from work (Zilberman, 1979).

The spectral transmission coefficient of the samples was measured on a spectrophotometer SF-46 in the range of wavelengths 200-1000 nm.

The refraction indes was determined by means of apparatus Anton Paar Abbemat 200.

The modification of co-BMA+St with nanoparticles of $Cu(CH_3COO)_2$ was carried out by means of device with rollers of small form №58 (plant ”Kostroma”).

3. Results and discussion

For revealing the dependence of the composition of copolymers on composition of the initial mixture of monomers, the copolymerization reaction was carried out at various molar ratios of BMA (M_1) and St (M_2) (Table 1). The molar fractions of the corresponding links m_1 and m_2 have been calculated on the basis of data of elemental and IR-spectral analyses.

Table 1. Copolymerization of BMA (M_1) with ST (M_2)

Composition of the initial mixture, mol.%		**Composition of copolymers, mol.%**		r_1	r_2	Q	e	**Microstructure of copolymer**		
M_1	M_2	m_1	m_2					L_{M_1}	L_{M_2}	R
90	10	86.45	13.55	0,64	0,54	Q_1=0.72 Q_2=1.00	e_1=-0.23 e_2=-0.80	6.76	1.06	25.57
75	25	71.22	28.78					2.92	1.18	39.21
50	50	51.57	48.43					1.64	1.54	62.89
25	75	31.65	68.35					1.21	2.62	52.17
10	90	15.45	84.54					1.07	5.86	28.86

$L_{M_1}$and L_{M_2} – average length of block of monomer units; R – Harwood coefficient

It was known that the copolymerization constants of BMA (M_1) and St (M_2) are close and below one (r_1=0.64 and r_2=0.54), i.e. at equal ratio the consumption rates of these monomers are practically the same. For conversion depths of 70-75%, the consumption of styrene is slightly decreased, which is explained by the limited solubility of styrene with forming copolymers. Consequently, this factor leads to the structural heterogeneity of the synthesized copolymers.

It has been established that (Table 1) the length of blocks L_{M_1} is increased with growth of molar fraction of BMA in the composition of copolymer. Blockness parameter R is decreased from 62.89% to 28.86% with increase of the length of block from 6.76 to 1.07 links. A maximum value of blockness parameter (R=69.88%) is reached at ratio of the initial monomers 0.5:0.5 (molar fraction).

BMA+St combining the advantages of both BMA and St have higher physical-mechanical and heat-physical properties in comparison with polystyrene and BMA. Indeed, it follows from the data shown in Table 2 that the copolymer has higher heat-physical and physical-mechanical properties in comparison with polystyrene, which do not give dangerous fragments during strikes. These qualities allow their using in making of details for optical devices and contact lenses.

Table 2. Physical-mechanical characteristics of the synthesized copolymer

Name of indices	п-Ст	БМА+Ст
Vicatheat resistance, °C	103	120
Brinell hardness, kg/mm^2	14	17
Specific impact strength, $kg \cdot cm/cm^2$	18	19
Tensile strength, MPa	39.0	70
Refraction index	1.5890	1.5870
Adhesion strength, MPa	-	5.4

Composition of copolymer of BMA:St 0,5:0,5.

The obtained results indicate that the copolymer of BMA+St along with high physical-mechanical characteristics also has good optical properties. It has been shown that BMA+St retains a transparency up to 100°C in its holding for 2 h. The investigation of physical-mechanical properties of BMA+St in the temperature interval from 80° to -20°C showed that at these temperatures it retains a higher tensile strength and doesn't practically decrease an elasticity in the field of low temperatures.

At the same time, the copolymer obtained on the basis of BMA+St has good optical properties (n_D^{20}=1.5870) in comparison with PMMA (1.491). Of course, these positive differences have been connected with the second and third structure of the copolymer.

The changes of some properties of copolymers of BMA +St depending on their composition are shown in Table 3.

Table 3. Properties of BMA+ST of different composition

Index	Content of BMA in copolymer, mol %			
	20	40	60	80
Tensile strength, MPa	70	72	75	79
Izod impact strength (3.2 mm), kJ·m^2	23	21	20	18
Melt flow index, 200°C: g/10 min.	1.2-2.1	0.7-1.2	0.5-0.6	0.4

The dependence of spectral transmission coefficient of BMA+St on composition and microstructure of the copolymer has been investigated (Fig.1).

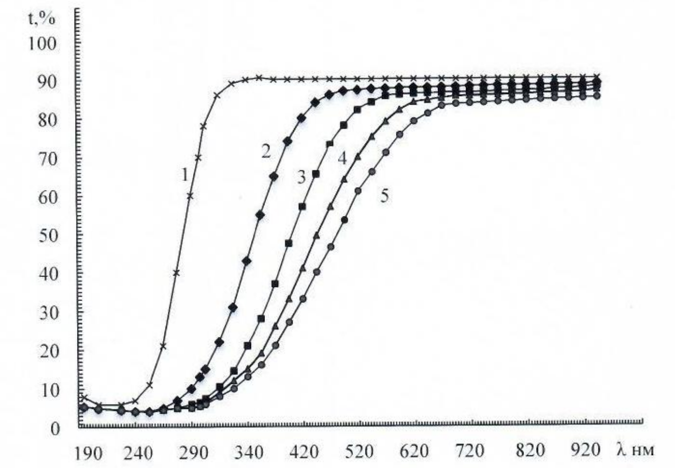

Figure 1. Spectral transmission coefficient of BMA+St.
BMA:St, mol. %: 0.9-0.1; 0.7-0.3; 1-1; 0.3-0.7; 0.1-0.9

For preparation of material with higher optical data, the obtained copolymer of BMA+St has been modified with nanoparticles of $Cu(CH_3COO)_2$. In comparison of BMA+St the modified BMA+St is differed with higher spectral transmission coefficient (Fig. 2).

The transparency of the modified BMA+St (light transmission in the visible part of the spectrum) is 90% and depends little on thickness of the sample up to 6-8 mm. At relatively high thicknesses, a partial deterioration of optical properties occurs, which is typical for all known transparent polymers. The high-quality optical products made from modified BMA+St can be obtained by pressing, extrusion and casting under pressure.

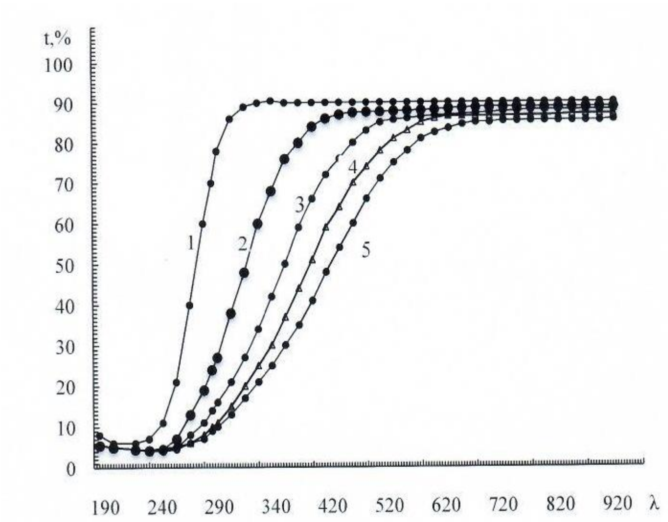

Figure 2. Spectral transmission coefficient of BMA+St and modified BMA+St, $Cu(CH_3COO)_2$ mol. %: 1 – 0; 2 – 0.10; 3 – 0.25; 4 – 0.5; 5 – 0.75.

Thus, it can be concluded analyzing obtained results that the copolymerization of BMA with St and in addition modification with nanoparticles of $Cu(CH_3COO)_2$ leads to the improvement of optical, heat-physical, adhesion, physical-mechanical and other properties of purposeful polymers and allows to obtain high-impact transparent polymer nanocomposites with high optical indices.

The copolymer obtained on the basis of monomers of BMA+St, modified by nanoparticles of $Cu(CH_3COO)_2$ show higher optical transparency(n_D^{20} =1,5940) than the copolymer of BMA+St (1.5870). Naturally this is connected with availability of nanoparticles of $Cu(CH_3COO)_2$ in the composite. The availability of nanoparticles leads to a change in the third structure of the polymer material from the copolymer of BMA+St, which positively influences on character of light quantization in the polymer nanocomposite. This nanocomposite has good light transmission (90%).

Thus, the results presented in Fig. 1 and Fig. 2 once again confirm that by purposefully modification of the second and third structures of the copolymers BMA+St one can essentially improve both the physical-mechanical and rheological, optical, and also heat-physical properties of the polymer material.

The developed copolymer is an optically transparent material for use in opto-technology, as well as in processes for making of optical lenses for microschemes.

4. Conclusions

It has been established that by copolymerization of butyl methacrylate with styrene one can obtain the optically transparent material with the best physical-mechanical properties. It has been revealed that the synthesized copolymer possess high optical transparency (n_D^{20} =1.5870). Copolymer butyl methacrylate with styrene has been modified by nanoparticles of $Cu(CH_3COO)_2$. The copolymer obtained on the basis of monomers of BMA+St, modified by nanoparticles of $Cu(CH_3COO)_2$ show higher optical transparency(n_D^{20} =1,5940) than the copolymer of butyl methacrylate with styrene (1.5870). A light transmission of the obtained composite (90%) is higher than in the copolymer BMA+St (88%).

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