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Optically transparent melamine-formaldehyde polymers modified with proton acceptors

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Investigation of reaction water binding in melamine-formaldehyde polymers with proton accepting compounds has shown that the use of dimethyl sulfoxide in 1/1 (v/v) ratio provides preparation of optically transparent materials. Introduction of dimethyl formamide and dimethyl sulfoxide improves the main characteristics of the material, but modification with dimethyl formamide reduces the polymer transparency.

Исследование процессов связывания реакционной воды в меламино-формальдегидных полимерах с помощью протонно-акцепторных соединений показало, что при использовании диметилсульфоксида в объемном соотношении 1:1 можно получить оптически прозрачные материалы. Введение диметилформамида и диметилсульфоксида улучшает основные характеристики материала, однако модификация диметилформамидом снижает прозрачность полимеров.

Optically transparent polymers are used widely in production of optical fibers, lens optics, lasers, light guides, scintillators, etc. [1]. The preparation of highly transparent polymers is a very difficult task requiring a combination of efficient purification of the initial monomers and optimized synthetic technique. The optical properties of a polymer are affected substantially by the polymer material purity and homogeneity (in composition, structure, chemistry, space, etc.) that define both its transparency and coloration as well as the refractive index inhomogeneity over the volume [2].

In [3–6], described is the preparation of translucent melamine-formaldehyde (MF) polymers having a high transparency coefficient, low residual stress, shrinkage, water absorption level and high physical and mechanical characteristics. However, the above-mentioned MF polymers have a much worse bulk light attenuation (BAL) value as compared to polystyrene and poly(methyl methacrylate) (20–25 cm against 50–200 cm). Apparently this is due to hydrophobic properties of the MF oligomers having the cross-linking extent above 50 % that causes some amount of reaction water to be retained in the hardened MF polymers. As a result, a micro-inhomogeneity appears at the MF polymer/water interface manifesting itself as a twisting that causes the light scatter and low BAL level.

It is known that dimethyl sulfoxide (DMSO), dimethyl formamide (DMFA), and pyridine may form associates with water molecules according to a mechanism discussed in [7]. In particular, DMSO forms a stable complex with water at the volume ratio DMSO/water 35/65 [8–10]. The purpose of this work is to study the water interactrion processes with proton accepting compounds (PAC) in the MF polymer matrix and the PAC influence on the optical and

Table 1. Main characteristics of PAC-modified MF polymers

Sample	Density, g/cm^3	Shrinkage, %	Water absorption, %	Bending failure strength, MPa	Impact strength, kJ/m^2	Cross-linking degree, %	Transparency coefficient, %
MF polymer	1.432	0.2	0.2	50	4.68	73	89
MF polymer + DMSO at the water:DMSO volume ratio							
2:1	1.3757	0.02	0.3	60	4	67	90
1:1	1.4032	0.015	0.5	135	7	64	95
1:1.5	1.5	0.01	0.9	65	6	60	92
MF polymer + DMFA at the water:DMF volume ratio							
2:1	1.4645	0.07	0.45	60	5.37	71	90
1:1	1.4824	0.02	0.35	59	3.72	68	93
1:1.5	1.5233	0.01	0.3	20	3.7	64	91
MF polymer + pyridine at the water:pyridine volume ratio							
2:1	1.4453	0.08	0.4	19	9.74	70	86
1:1	1.4665	0.02	0.2	7	6.85	66	88
1:1.5	1.5034	0.02	0.25	6	3.42	62	84

spectral characteristics of materials so obtained. A study directed to elimination of negative effect of reaction water on the optical and spectral properties of MF polymers by its chemical binding is no doubt of a scientific and practical interest.

The MF oligomers were prepared as in [3]. DMSO, DMFA, and pyridine were used in this work to bind the reaction water. The MF polymers were studied with the water:PAC volume ratio of 2:1, 1:1, and 1:1.5. The transparency coefficient of the MF polymers was estimated using the intrinsic absorption spectra in the 190–900 nm range obtained with a Hitachi U2310 spectrophotometer. The BAL was determined by laser spectrometry using a He–Cd laser (λ = 441 nm). A SPECORD 75 UR spectrophotometer was used in IR spectroscopy experiments. Thermographic analysis of polymers was carried out using a Q-1500D derivatograph (MOM, Hungary). Other physical and physicochemical characteristics were determined according to standards and procedures described in [11, 12]. The moisture content in the polymer samples was determined using the titrimetric K.Fischer technique as the arbitrary one according to the procedure described in [13]. The water was extracted from the sample to dried methanol under stirring with a magnetic stirrer for 3 h. The working solution of the K.Fischer reagent, standard water solution in methanol and the background dye (methylene blue) solution were prepared according to [13]. The titration with visual determination of the equivalence point was carried out in a setup providing the reagent and sample protection against the atmospheric moisture [14].

In Table 1, presented are the main physical and mechanical properties of the MF polymers modified with different PACs. The effect of a PAC on the main polymer characteristics is seen to depend on the PAC type and water:PAC volume ratio. The highest transparency coefficients are characteristic for the MF polymers modified with DMSO (90–95 %) and DMFA (90–93 %), the optimum water:PAC volume ratio being 1:1. In all the modified MF polymers, the shrinkage decreases and water absorption rises as the PAC content increases. The DMSO modified polymers show a decreased density while the modification with other two PACs results in an increased density. The data from the Table confirm that the MF polymers with the water:PAC volume ratio 1:1 show the best physical-mechanical properties. Both impact strength and failure bending stress become reduced as the above-mentioned ratio increases or decreases as well as when two ther PACs are used. Taking into account that highest transparency coefficients (up to 95 %) and BAL values (60 cm) were attained in the DMSO modified MF polymers, the water material balance in those MF oligomers and polymers was studied using the gravimetry and thermogravimetry as well as the K.Fis-

Table 2. Material balance of water (wt %) in DMSO-modified MF polymers and oligomers

Sample	Water, wt %						
	Evaporated from oligomer	Released as surface moisture	In polymer prior to annealing (K.Fischer)	Removed at the polymer annealing	Introduced with DMSO	Calculated in polymer	Found by K.Fischer techn.
MF Polymer	3.1±0.1	0.19±0.04	8.9±0.8	4.2±0.1	0	5±1	4.6±0.3
Polymer with DMSO (2:1)	2.2±0.2	0	N.D.	4.0±0.1	0.026±0.002	6±1	4.9±0.5
Polymer with DMSO (1:1)	2.1±0.1	0	N.D.	3.9±0.2	0.049±0.005	7±1	3.3±0.3
Polymer with DMSO (1:1.5)	2.3±0.1	0	N.D.	4.4±0.1	0.069±0.006	6±1	5.9±0.5

cher titration (see Table 2) to determine quantitatively the water binding.

It is seen from Table 2 that in the MF polymers with water:DMSO volume ratio 1:1, at the actual water content of 7 + 1 wt. %, the K.Fischer titration shows the water amount of 3.3 + 0.3 wt. % (47.1 % of free water in relative units). As the water:DMSO volume ratio is increased up to 2:1, at the actual water content of 6 + 1 wt. %, 4.9 + 0.5 wt. % (81.6 % of free water) has been found while as the above ration is decreased down to 1:1.5, at the actual water content of 6 + 1 wt. %, the found water amount is 5.9 + 0.5 wt. % (98.3 % of free water). Water is bound most efficiently in the MF polymers with water:DMSO volume ratio 1:1 due to formation of a stable water-DMSO complex. This is confirmed by consideration of IR spectra of the MF polymers with different water:DMSO ratios in the characteristic absorption region (3,000 to 3,700 cm^{-1}) of bound and free water.

Thus, the use of pyridine as a modifier of MF oligomers has been shown to impair the properties of MF polymers while the DMSO and DMF introduction enhances the main characteristics thereof. However, the DMF modification does not provide optically transparent MF polymers with satisfactory physical-mechanical properties. The polymer materials prepared from MF oligomers with water:DMSO volume ratio 1:1 show at the best physical-mechanical properties. the transparency coefficient of 95 % and BAL of 60 cm. This makes it possible to use the materials in lens optics, scintillation engineering, and in other applications requiring materials of high optical quality.

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Оптично прозорі меламіно-формальдегідні полімери, що модифіковані протоноакцепторними сполуками

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Дослідження процесів зв'язування реакційної води у меламіно-формальдегідних полімерах за допомогою протоноакцепторних сполук показало, що при застосуванні диметилсульфоксиду в об'ємному співвідношенні 1:1 можна одержати оптично прозорі матеріали. Введення диметилформаміду та диметилсульфоксиду покращує основні характеристики матеріалу, однак модифікація диметилформамідом знижує прозорість полімерів.