CHEMISTRY AND TECHNOLOGY OF ORGANIC SUBSTANCES, MATERIALS AND GOODS

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PREPARATION AND STUDY OF PHYSICOCHEMICAL PROPERTIES OF MODIFIED ROSINS AND MODEL COMPOUNDS BASED ON THEM

Results of research of the modeling structures received with use of modified rosin are given in the article. It is shown that depending on the applied modifiers of rosin and conditions it is possible to make modeling structures with a wide range of physical-mechanical and operational properties. The use of modified rosin in model compositions opens up wide prospects for the development and production of new model compositions at the chemical plants of Belarus.

Introduction. The members of the laboratory of organic catalysis of SSI Physical-Organic Chemistry Institute of Belarus NAS and the Department of BSTU have been studying for several years [1] the modifying rosin (R) and its use in model compositions (MC) for precision casting.

In manufacturing technology models the exceptional acquires the problem of increasing technological and operational characteristics of MC, which requires new approaches to the selection of ingredients and creating a more effective compositions based on them.

In the Republic of Belarus a promising direction is to use as ingredients of MC secondary products of rosin or modified rosin (MR). As an analogy, let us consider the model compositions of brands ZGV-101 and ZGV-103 [2].

Main part. To improve the performance properties of pine rosin by chemical modification of the original R, the methods of R disproportionation and R condensation by paraformaldehyde were used [3].

To obtain the modified rosins the following materials were used: pine turpentine rosin (PTR) (JSC "Lesokhimik" batch No. 53, T_m = 73°C, AN = = 172 mg KOH/g), disproportionation rosin (DTR), T_m = 62°C, AN = 162 mg KOH/g and oleoresin pine rosin (PFPTR), modified 3 wt % paraformaldehyde (PF), T_m = 78°C, AN = 169 mg KOH/g.

Rosin composition is shown in Table 1.

The chemical compositions of the PTR, DTR, and PFPTR were established by NMR (Nuclear Magnetic Resonance) ^{1}H and ^{13}C [4, 5] in IPOCH NAS B. All samples were dissolved in $CDCl_3$ (10% solution). All the spectra were recorded on AVANCE-500 NMR spectrometer (operating frequencies of 500 MHz for ^{1}H nuclei and 125 MHz for ^{13}C). Chemical shifts of the proton signals of the compounds were determinate by a signal $CHCl_3$ (δ = 7.27 ppm, impurity $CDCl_3$), and ^{13}C chemical shifts were measured relatively to the solvent signal (δ = 7.77 ppm).

Table 1

Rosin Composition

Composition	PTR, %	DTR, %
Dehydroabietic acid	3.1	79.8
Neoabietic acid	16.2	0.1
Isopimaric acid	5.4	5.3
Abietic acid	34.5	3.2
Pimaric acid	9.2	4.3
Levopimaric acid	1.4	0.5
Palustric acid	24.1	2.1

For identification and quantitative determination of resin acids their individual spectra were recorded. I_2 served as disproportionation catalyst in the amount 0.1, 0.25 and 0.5 wt % (reaction temperature T = = 220±5°C, the reaction time τ = 2 h). Modifying PTR by paraformaldehyde was carried out at temperature T = 180±5°C, the reaction time τ = 3 h. Ethanolamine (EA), diethanolamine (DEA) and triethanolamine (TEA) were used as chemical modifiers.

Conditions to prepare the modified rosins are shown in Table 2.

Table 2

Conditions for preparing modified rosins

Sample number	Preparation conditions			
	Material	Modifier, wt %	*T*, °C	τ, h
1	PTR	20 EA	110–120	1
2	PTR	33 DEA	110–120	1
3	PTR	50 TEA	110–120	1
4	DTR	20 EA	110–120	1
5	DTR	33 DEA	110–120	1
6	DNR	50 TEA	110–120	1
7	PFPTR	20 EA	110–120	1
8	PFPTR	33 DEA	110–120	1
9	PFPTR	50 TEA	110–120	1

Alkanolamines [6] are colourless viscous hygroscopic liquid with a specific amine odour, miscible with water, freely soluble in ethanol, benzene, chloroform, hardly soluble in heptane. Alkanolamines possess the properties of amines and alcohols, they are weak bases. Alkanolamines react with carboxylic acids or anhydrides to form thermostable salts in the temperature range 80–140°C. The resulting alkanolamine salts are viscous product having an acid number (AN) = 2–4 mg KOH/g.

Compositions of the prepared MC for precision castings are shown in Tables 3 and 4, respectively.

While preparing the laboratory samples of the operating model compounds we used the following materials:

– Solid petroleum paraffin brands T-1, P-1, P-2 [7];
– Ceresin oil brand 80H [8];
– Polyethylene wax PW-200 [9];
– Lignite wax “Romonta” [10];
– PTR [11];
– DTR;
– PFPTR.

Experimental model compositions were prepared as follows:

– loading paraffin wax into the reactor and melting at 80–85°C;
– loading ceresin into the reactor and melting at 85–90°C;
– loading lignite wax into the reactor and melting at 85–90°C;
– loading the modified rosin into the reactor and melting at 90–95°C;
– loading of the polyethylene wax in the reactor and melting at 95–100°C;
– homogenization of the model composition at 95–100°C;
– drainage of the finished product.

MR samples were used to make a series of laboratory sample MC for precision casting, which serve as an analogue for MC brand ZGW-101 and ZGW-103 containing PTR, modified TEA.

The prepared experimental samples MC were tested in the laboratory according to the expanded range of indicators in the BSTU laboratories [12]. Bench tests of the MC samples were carried out in GSC “Mineral wax plant”.

Table 5 shows the properties of the developed MC based on the basic brand ZGW-101.

Table 3

Formulation of model compounds of ZGW-101 type

Number	Sample nomenclature	Paraffin T-1, wt %	PW-200, wt %	“Romonta”, wt %	Modified rosin, wt %
1	ZGW-101 R	45	10	30	15 PTR
2	ZGW-101 EA	45	10	30	15 (sample 1)
3	ZGW-101 DEA	45	10	30	15 (sample 2)
4	ZGW-101 TEA (basic)	45	10	30	15 (sample 3)
5	MC-D	45	10	30	15 DTR
6	MC-42 EA	45	10	30	15 (sample 4)
7	MC-44 DEA	45	10	30	15 (sample 5)
8	MC-41 TEA	45	10	30	15 (sample 6)
9	MC-PF	45	10	30	15 PFPTR
10	MC-45 EA	45	10	30	15 (sample 7)
11	MC-46 DEA	45	10	30	15 (sample 8)
12	MC-47 TEA	45	10	30	15 (sample 9)
13	MC-50	46.6	11.7	31.7	10 (6.75 wt % DTR + 3.25 wt % TEA)
14	MC-51	45	10	30	15 (10 wt % DTR + 5 wt % TEA)
15	MC-52	43.4	8.3	28.3	20 (13.5 wt % DTR + 6.5 wt % TEA)

Table 4

Formulation of model compounds of ZGW-103 type

Number	Sample nomenclature	Paraffin T-1, wt %	PW-200, wt %	"Romonta", wt %	Ceresin, wt %	Modified rosin, wt %
16	ZGW-103 R	35	7	28	15	15 PTR
17	ZGW-103 REA	35	7	28	15	15 (sample 1)
18	ZGW-103 RDEA	35	7	28	15	15 (sample 2)
19	ZGW-103 RTEA (basic)	35	7	28	15	15 (sample 3)
20	ZGW-103 D	35	7	28	15	15 DTR
21	ZGW-103 DEA	35	7	28	15	15 (sample 4)
22	ZGW-103 DDEA	35	7	28	15	15 (sample 5)
23	ZGW-103 DTEA	35	7	28	15	15 (sample6)
24	ZGW-103 PF	35	7	28	15	15 PFPTR
25	ZGW-103 PFEA	35	7	28	15	15 (sample 7)
26	ZGW-103 PFDEA	35	7	28	15	15 (sample 8)
27	ZGW-103 PFDEA	35	7	28	15	15 (sample 9)
28	MC-53	35	7	28	15	15 DTR_{573}
29	MC-54	35	7	28	15	15 DTR_{574}

Note. DTR_{573} – disproportionation rosin obtained at presence of 0.1% I_2; DTR_{574} – disproportionation rosin obtained at presence of 0.25% I_2.

As it can be seen from Table 5, the first series of compositions contain PTR. Modification PTR EA displays high performance properties of new MC: specific impact strength of the sample – 1.188 kg·sm/sm^2, linear shrinkage – within 1%, tensile strength at break – 4.79 MPa, bending stress – 8.98 MPa. MC tests showed that the PTR EA and DEA modifications significantly altered the viscosity properties of the composition: the melt flow index (MFI) decreases more than 10 times. However, the physical and mechanical properties of MC such as the specific impact strength, tensile strength and bending stress are only marginally affected. Modification PTR TEA decreases MFI by 25%, while the specific impact strength and tensile strength is almost not changed, and the bending stress is reduced by 35%.

Table 5

Complex operational MC properties of ZGW-101 type

Series number	Number	Sample nomenclature	Melt Flow Index (MFI), g/10 min	Specific impact strength, a, kg cm/cm^2	Shrinkage, (Shr), %	Dropping temperature, T_d, °C	Fluidity limit, σ_m, MPa	Tensile strength, σ_p, MPa	Bending stress, σ_b, MPa
1	1	WGF-101 R	4.64	990	0.87–1.05	93.0	3.92	3,2	8.39
	2	ZGW-101 EA	0.39	1,188	1.05–1.17	92.0	4.79	4.79	8.98
	3	ZGW-101 DEA	0.34	1,180	1.11–1.36	88.0–88.5	4.49	4.29	6.72
	4	ZGW-101 TEA	3.12	1,063	0.86–1.24	88.0–89.0	3.46	3.46	5.47
2	5	MC-D	2.84	1,041	1.3–1.79	88.5	4.86	4.86	8.46
	6	MC-42 EA	1.7	1,061	1.11–1.55	87.5	3.50	3.87	7.09
	7	MC-44 DEA	2.24	1,256	1.3–1.92	91.0	3.70	3.67	5.67
	8	MC-41 TEA	2.92	1,007	0.93–1.67	87.5–88.0	3.57	2.89	4.87
3	9	MC-PF	0.44	956	0.68–1.11	86.5–87.0	4.33	3.05	4.14
	10	MC-45 EA	0.56	1,134	1.32	89.0–90.0	3.61	2.66	6.06
	11	MC-46 DEA	0.46	998	0.99–1.57	88.0–90.0	3.75	3.75	7.24
	12	MC-47 TEA	0.64	1,025	0.87	89.0	3.61	2.81	6.08
4	13	MC-50	0.54	804	2.023	94.0–94.5	3.30	3.30	1.56
	14	MC-51	0.5	729.3	1.821	87.0	2.05	2.24	2.25
	15	MC-52	0.52	436.3	1.59	86.0–86.5	2.51	2.51	2.42

The second series of compositions contain DTR. Experiments have shown that modification DTR DEA has secured the optimal values of the following indicators: MFI – 2.24 g/10 min, specific impact strength of the sample – 1.256 kg·sm/sm^2, linear shrinkage – within 1.3% (it is regulated by processing methods such as decreasing the rate of cooling of the composition), tensile strength at break – 3.67 MPa, bending stress – 5.67 MPa.

Increasing the molecular weight of the modifier with EA from 61.08 till 105.14 at with DEA helps to reduce MFI of the sample, and then restore the previous value of the indicator in the case of TEA, having a molecular weight 149.19. Specific impact strength of the compositions is almost unchanged, tensile strength decreases by 40% in the case of TEA, wherein the bending stress is also reduced by 42.5%.

The third series of compositions contains PFPTR. Comparison of properties of the MC showed the preferential use as a chemical modifier PFPTR DEA and TEA. Compositions number 11 and 12 have low shrinkage (less than 1%), high bending stress values (7.24 and 6.08 MPa, respectively). Sample number 11 of MC is inferior to number 12 on the viscosity characteristics (MFI 0.46 and 0.64 g/10 min, respectively).

Modification of PFPTR by ethanolamines increases MFI by 18%, while the specific impact strength of the samples remains almost unchanged. Tensile strength at break of the MC series specimen varies within ±18%.

Increase of MR in compositions No. 13–15 leads to reduction of the specific impact strength, linear shrinkage and MFI of MC samples. The value of the bending stress of the investigated MC samples increases by 55%, but the absolute value of it is greatly inferior to the same index of samples No. 1–12 (Table 5).

Using DTR instead of PTR increases MFI of model composition, the tensile strength of MC at break slightly increases. Correlation values of the specific impact strength and the bending stress in the laboratory samples of each series were not found.

Table 6 shows the properties of MC developed on the basic of ZGW-103 type.

In the first series of compositions PTR was used (Table 4). The use as a modifier PTR EA increases the bending stress of MC samples by 23% (4.11 MPa). Modification of the original composition of DEA and TEA does not give advantages over the analogue. Increasing the molecular weight of the modifier reduces the tensile strength properties of the MC samples within 50%. Shrinkage of samples exceeds 2%.

The second series of compositions contains DTR. Increase of the bending stress of the MC sample by 34–59% was observed in modifying DTR by any alkanolamine. Specific impact strength of the modified samples practically is unchanged. Use of EA in the composition as a modifier provides the highest value of the bending stress (4.0 MPa). The linear shrinkage value is more preferable with the modifiers EA (1.778%), and TEA (1.852%). TEA modifier degrades the tensile strength characteristics of MC samples. In this series of samples, the smallest value of the linear shrinkage (1.596%) is observed in the initial sample.

Table 6

Complex operational MC properties of ZGV-103 type

Series number	Number	Sample nomenclature	Specific impact strength, a, kg·cm/cm^2	Shrinkage, (Shr) %	Dropping temperature, T_d, °C	Fluidity limit, σ_m, MPa	Tensile strength, σ_p, MPa	Bending stress, σ_b, MPa
1	1	ZGW-103 R	695	1.721	78.0–79.0	4.20	4.18	3.34
	2	ZGW-103 REA	607.9	1.8156	86.5–87.0	3.94	3.94	4.11
	3	ZGW-103 RDEA	504.45	2.976	88.0–88.5	2.61	2.44	2.96
	4	ZGW-103 RTEA	591.4	2.0128	90.0–90.5	1.80	1.19	1.93
2	5	ZGW-103 D	460.85	1.596	86.5–86.0	3.85	3.63	2.52
	6	ZGW-103 DEA	470.8	1.778	90.5–91.0	3.27	2.49	4.00
	7	ZGW-103 DDEA	479.0	2.496	86.0–86.5	3.26	3.26	3.66
	8	ZGW-103 DTEA	437.4	1.852	86.0	1.63	1.43	3.11
3	9	ZGW-103 PF	191.419	1.467	87.0	2.01	1.79	5.84
	10	ZGW-103 PFEA	282.97	1.4345	87.5–88.0	2.38	1.89	3.21
	11	ZGW-103 PFDEA	241.01	1.669	86.5–87.0	2.90	2.85	4.44
	12	ZGW-103 PFDEA	368.94	1.742	86.5–87.0	2.34	1.78	2.74
4	13	MC-53	296.6	2.0375	94.0	2.23	1.60	1.95
	14	MC-54	374.5	2.204	98.0	2.06	2.11	2.79

The third series of compositions contains the rosin modified by PF. Specific impact strength of the samples increases from 26 to 92% with increasing amount of alkanolamine groups. The magnitude of tensile strength at break and the bending stress in the series of samples prefers the DEA modifier: 2.85 and 4.44 MPa, respectively.

In this series of samples linear shrinkage is more than 1.5%. The highest value of the specific impact strength index has a sample modified by TEA – 368.94 MPa.

When comparing a series of samples for the strength properties it can be noted that the first and second series are competitive in terms of tensile strength at break and bending stress. The second series of samples is slightly inferior to the specific impact strength values of first series samples. Samples of the third series have comparable values of linear shrinkage and bending stress with samples of the first two series.

Methods of DTR preparation as an ingredient of model compositions significantly affect the strength properties of the developed MC. Thus, increasing 2.5 times catalyst content in the synthesis of disproportionated rosin promotes increasing the tensile strength at break, bending stress, and specific impact strength of the compositions. Note, however, that the samples number 13 and 14 have a linear shrinkage of more than 2%.

Conclusion. The chemical modification of rosin, the most important MC component for precision casting, allowed compiling the compositions superior in a number of basic properties of MC brands ZGW-101 and ZGW-103.

Comparative evaluation of performance properties of the MC complex of 27 new and 2 basic ones allowed us to reliably determine the best of them: ZGW-101 EA; ZGW-101 DEA; MC-44 DEA, MC-46 DEA; MC-47 TEA; ZGW-103 REA; ZGW-103 DEA; ZGW-103 PFDEA; ZGW-103 PFTEA.

In developing the MC formulations DTR and PFPTR should be preferred as rosin component formulations.

The developed MC samples were sent for additional testing to the “Mineral wax plant”.

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