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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Modification with Maleic Acid of the Copolymer from By-Products of Polybutadiene Production and Use of the Modified Copolymer for Protective Treatment of Wood Fiberboards

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Abstract—Modification with maleic acid of a styrene-containing polymeric material prepared from by-products of polybutadiene production was studied.

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Many wastes from petrochemical enterprises, including synthetic rubber plants, contain numerous reactive compounds.

It is known that butadiene dimers and trimers, on the one hand, are by-products in some petrochemical processes involving butadiene and, on the other hand, can be valuable raw materials for various organic and petrochemical syntheses and for production of polymeric materials [1, 2]. A process for production of styrene-containing low-molecular-weight polymeric materials from these by-products has been commercially implemented [3, 4]. However, the polymeric materials thus obtained contain no functional groups, which restricts their possible applications.

The problems of chemical modification of synthetic polymers, rubber stocks, and vulcanizates are given much attention today from both scientific and practical viewpoints. Introducing functional groups into the copolymers and finding new fields of their applications are important problems.

In this study, we examined the possibility of using for impregnation of wood materials a low-molecular-weight copolymer prepared from unsaturated compounds of recycled toluene distillation bottoms (TDB) from polybutadiene production, modified with maleic acid (MA). The interest in maleic acid as a modifying agent is based on the fact that maleic acid is a by-product in the production of phthalic and maleic anhydrides. Therefore, this process not only allows modification of polymeric materials prepared from by-products of polybutadiene production, with new properties imparted to the resulting compounds, but also provides utilization of production waste.

Maleic (*cis*-butenedioic) acid can be dehydrated to obtain maleic anhydride. Maleic acid and its esters readily isomerize into fumaric acid and its derivatives under the action of heat, light, and catalysts. Maleic acid is widely used for preparing various surfactants. Certain amount of MA is used in food industry for preparing tartaric acid [5].

EXPERIMENTAL

We examined how the MA content of the reaction mixture, temperature, and process duration affect the properties of the styrene-containing polymeric material based on unsaturated TDB (bound styrene content 75–80 wt %).

The modification was performed as follows. A reactor was charged with 100 g of 70% toluene solution of a low-molecular-weight styrene-containing polymeric material based on unsaturated TDB, and MA was added in various ratios to the starting polymer. The best modification conditions were determined by using the method of experiment design. We examined the effects of such factors as MA content, temperature, and process duration using the 4 × 4 Latin square plan [6]. For each factor, we took four levels of variation: factor A (MA dosage), 0, 3.0, 6.0, and 9.0 wt %; factor B (process temperature), 120, 150, 180, and 210°C; and factor C (process duration), 8, 16, 24, and 32 h. The reaction progress was monitored by analytical methods from the variation of the mean molecular

Table 1. Plan and results of the experiment*

A, wt %	B, °C			
	b_1 = 120	b_2 = 150	b_3 = 180	b_4 = 210
a_1 = 0	c_1 = 8 h y_1 = 1540 y_1' = 18.4 y_1'' = 1.2	c_2 = 16 h y_2 = 1570 y_2' = 17.8 y_2'' = 2.9	c_3 = 24 h y_3 = 1890 y_3' = 17.0 y_3'' = 2.4	c_4 = 32 h y_4 = 1580 y_4' = 16.2 y_4'' = 1.7
a_2 = 3	c_2 = 16 h y_5 = 1700 y_5' = 17.8 y_5'' = 8.1	c_3 = 24 h y_6 = 1920 y_6' = 16.9 y_6'' = 15.3	c_4 = 32 h y_7 = 1570 y_7' = 16.0 y_7'' = 11.4	c_1 = 8 h y_8 = 1820 y_8' = 15.1 y_8'' = 7.5
a_3 = 6	c_3 = 24 h y_9 = 1650 y_9' = 16.1 y_9'' = 8.8	c_4 = 32 h y_{10} = 2190 y_{10}' = 15.7 y_{10}'' = 5.6	c_1 = 8 h y_{11} = 1400 y_{11}' = 15.5 y_{11}'' = 13.1	c_2 = 16 h y_{12} = 2010 y_{12}' = 14.9 y_{12}'' = 9.7
a_4 = 9	c_4 = 32 h y_{13} = 1840 y_{13}' = 14.7 y_{13}'' = 13.4	c_1 = 8 h y_{14} = 2380 y_{14}' = 15.3 y_{14}'' = 6.7	c_2 = 16 h y_{15} = 2320 y_{15}' = 14.0 y_{15}'' = 11.3	c_3 = 24 h y_{16} = 2830 y_{16}' = 13.7 y_{16}'' = 15.5

* (y_i) Molecular weight; (y_i'), bromine number, (g Br$_2$) (100 g)$^{-1}$; and (y_i'') acid number, (mg KOH) g^{-1}.

weight $\overline{M}_v$ and of the acid and bromine numbers, which were determined in reaction mixture samples taken at regular intervals. The matrix of the Latin square plan is shown in Table 1.

Based on the experimental results, we plotted (Fig. 1) the dependences of the modification results on the above factors and obtained the regression equations. The equations of the dependences of the mean

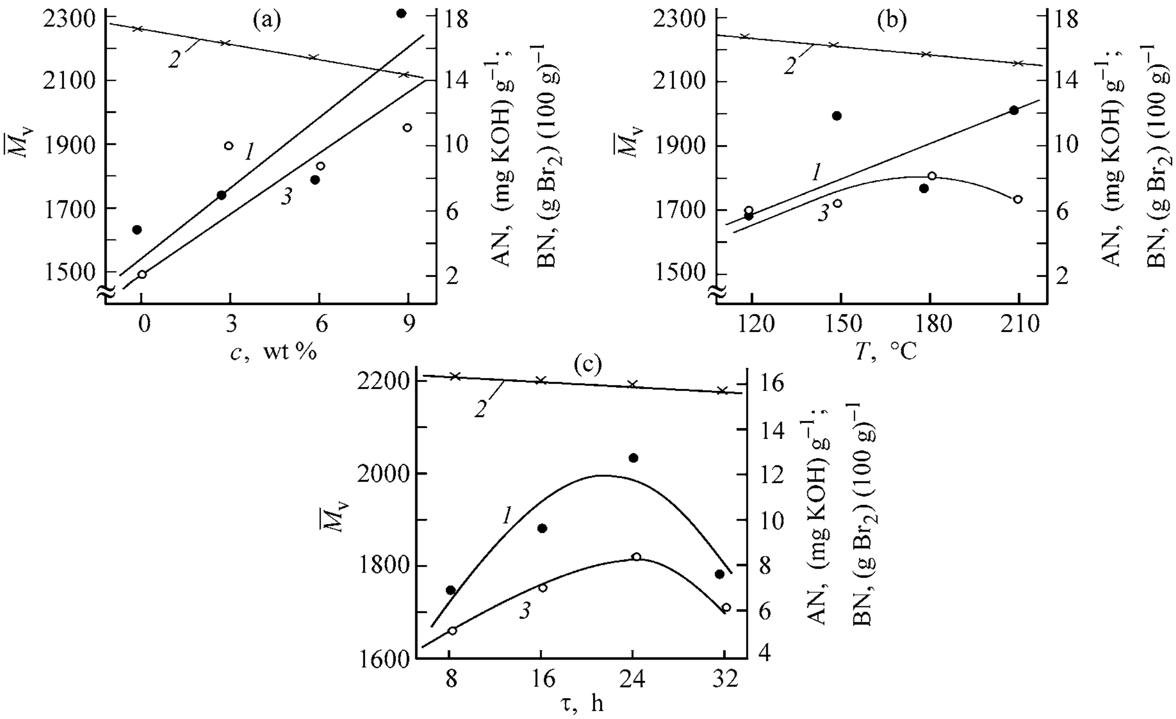


Fig. 1. Influence of (a) MA content c (0, 3.0, 6.0, 9.0 wt %, factor A), (b) process temperature T (120, 150, 180, 210°C, facotr B), and (c) process duration τ (8, 16, 24, 32 h, factor C) on (*1*) mean molecular weight $\overline{M}_v$, (*2*) bromine number BN, and (*3*) acid number AN.

Table 2. Plan and results of the experiment*

A, s	B, °C			
	$b_1 = 25$	$b_2 = 50$	$b_3 = 75$	$b_4 = 100$
$a_1 = 30$	$c_1 = 1$ h $d_1 = 120$°C $y_1 = 32.7$ $y_1' = 20.6$ $y_1'' = 14.5$	$c_2 = 3$ h $d_2 = 140$°C $y_2 = 36.6$ $y_2' = 19.1$ $y_2'' = 13.9$	$c_3 = 5$ h $d_3 = 160$°C $y_3 = 40.7$ $y_3' = 17.8$ $y_3'' = 13.8$	$c_4 = 7$ h $d_4 = 180$°C $y_4 = 49.8$ $y_4' = 16.9$ $y_4'' = 11.3$
$a_2 = 60$	$c_2 = 3$ h $d_3 = 160$°C $y_5 = 35.1$ $y_5' = 18.9$ $y_5'' = 13.4$	$c_1 = 1$ h $d_4 = 180$°C $y_6 = 37.9$ $y_6' = 18.1$ $y_6'' = 14.2$	$c_4 = 7$ h $d_1 = 120$°C $y_7 = 32.0$ $y_7' = 18.6$ $y_7'' = 14.5$	$c_3 = 5$ h $d_2 = 140$°C $y_8 = 41.2$ $y_8' = 17.2$ $y_8'' = 12.7$
$a_3 = 90$	$c_3 = 5$ h $d_4 = 180$°C $y_9 = 53.1$ $y_9' = 18.0$ $y_9'' = 11.6$	$c_4 = 7$ h $d_3 = 160$°C $y_{10} = 48.9$ $y_{10}' = 17.9$ $y_{10}'' = 12.4$	$c_1 = 1$ h $d_2 = 140$°C $y_{11} = 39.3$ $y_{11}' = 17.0$ $y_{11}'' = 13.1$	$c_2 = 3$ h $d_1 = 120$°C $y_{12} = 34.6$ $y_{12}' = 17.0$ $y_{12}'' = 12.9$
$a_4 = 120$	$c_4 = 7$ h $d_2 = 140$°C $y_{13} = 45.3$ $y_{13}' = 17.5$ $y_{13}'' = 12.1$	$c_3 = 5$ h $d_1 = 120$°C $y_{14} = 39.5$ $y_{14}' = 17.2$ $y_{14}'' = 11.7$	$c_2 = 3$ h $d_4 = 180$°C $y_{15} = 44.8$ $y_{15}' = 16.9$ $y_{15}'' = 11.2$	$c_1 = 1$ h $d_3 = 160$°C $y_{16} = 40.2$ $y_{16}' = 16.5$ $y_{16}'' = 10.9$

* (y_i) Bending strength, MPa; (y_i') water absorption in 24 h, %; (y_i'') swelling in thickness in 24 h, %.

molecular weight and of the bromine and acid numbers on the above factors are as follows:

for the molecular weight $\overline{M}_v$,

$$Y = 2.92 \times 10^{-7}$$
$$\times (1562 + 69a)(1439 + 2.6b)(1322 + 63c - 1.5c^2);$$

for the bromine number, (g Br_2) $(100\ \mathrm{g})^{-1}$,

$$Y' = 3.96 \times 10^{-3}(17.34 - 0.32a)$$
$$\times (19.31 - 2.07 \times 10^{-2}b)(16.22 - 1.625 \times 10^{-2}c);$$

and for the acid number, (mg KOH) g^{-1},

$$Y'' = 2.32 \times 10^{-2}(4.07 + 0.884a)$$
$$\times (-9.48 + 0.19b - 5.367 \times 10^{-4}b^2)$$
$$\times (0.708 + 0.682c - 1.58 \times 10^{-2}c^2).$$

Thus, an increase in the MA content and temperature leads to a rise in the mean molecular weight of the product, described by first-order equations. This fact can be attributed to the cross-linking in the system through Diels–Alder addition of MA to the macromolecules [7] and addition of MA to sites of double bond cleavage in the polymeric chains. It is important that MA can behave at high temperatures as a cationic catalyst and can accelerate the cross-linking. The influence of the reaction duration on the modification can be described by a second-order equation with a maximum, indicating that degradation processes become prevalent after approximately 20 h.

The acid number steadily grows with an increase in the MA content of the reaction mixture. However, the influence of the temperature and process duration on the acid number is described by second-order equations with maxima. This may be due to partial dehydration of MA and its transformation into maleic anhydride. The extent of this process increases with temperature. It is known that active dehydration of MA starts at ≥130°C, and at 150°C an equilibrium with 50% conversion is attained in 0.3 h [5, 8].

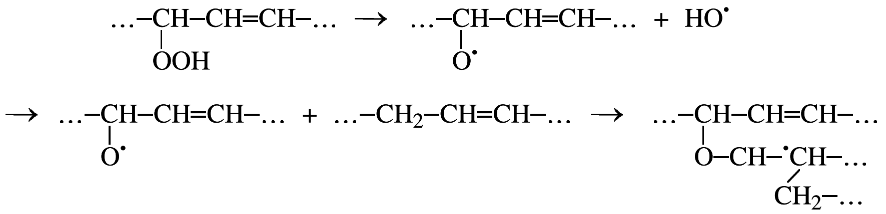
Thus, by varying the MA content, process duration, and temperature, it is possible to control the properties of the resulting products so as to meet consumer's requirements.

Functionalization of the styrene-containing polymeric material prepared from by-products formed in polybutadiene production opens new prospects for its application, such as production of rubber by emulsion (co)polymerization and protective treatment of wood materials with the aim to enhance their resistance to water and moisture and their mechanical strength.

We examined the application of the MA-modified product to treatment of wood fiberboards (WFBs). In so doing, we used the fourth-order 4 × 4 Greco-Latin square plan [6]. As the major factors exerting the strongest effect on the WFB properties we chose the impregnation duration (factor A; 30, 60, 90, 120 s), impregnating formulation temperature (factor B; 25, 50, 75, 100°C), heat treatment temperature (factor C; 120, 140, 160, 180°C), and heat treatment time (factor D; 1, 3, 5, 7 h). The following WFB parameters were monitored: bending strength, water absorption, and swelling in thickness. The matrix of the Greco-Latin square plan is given in Table 2.

The WFB treatment was performed as follows. Dried and weighed specimens were placed in an impregnation bath containing a polymeric material modified with MA, with addition of ~10 wt % drier, and kept for a prescribed time at a prescribed temperature according to the experimental plan. For impregnation we took the polymeric material modified with 6.0 wt % MA for 24 h. The impregnated WFB specimens were withdrawn from the bath, predried, and subjected to a heat treatment, after which they were cooled to room temperature and weighed. The copolymer content of the specimens was determined gravimetrically from the weight gain.

Addition of a drier accelerates both formation and decomposition of hydroperoxides. The reactions involving atmospheric oxygen actively occur in the surface layers. The oxygen access into the bulk of the formulation is limited, which leads to decreased contribution of oxidative processes and increased contribution of high-temperature polymerization. The last process is activated by various radicals present in the system ($R^{\cdot}$, $RO^{\cdot}$, $ROO^{\cdot}$, see scheme).



$$\ldots-\underset{\substack{|\\ \mathrm{OOH}}}{\mathrm{CH}}-\mathrm{CH{=}CH}-\ldots \longrightarrow \ldots-\underset{\substack{|\\ \mathrm{O^{\bullet}}}}{\mathrm{CH}}-\mathrm{CH{=}CH}-\ldots + \mathrm{HO^{\bullet}}$$

$$\longrightarrow \ldots-\underset{\substack{|\\ \mathrm{O^{\bullet}}}}{\mathrm{CH}}-\mathrm{CH{=}CH}-\ldots + \ldots-\mathrm{CH_2}-\mathrm{CH{=}CH}-\ldots \longrightarrow \ldots-\underset{\substack{|\\ \mathrm{O-CH-{}^{\bullet}CH-\ldots}\\ \diagup\\ \mathrm{CH_2-\ldots}}}{\mathrm{CH}}-\mathrm{CH{=}CH}-\ldots$$

The film formation is inevitably accompanied by oxidative degradation yielding compounds that contain carbonyl, carboxy, and hydroxy groups. This leads to a further increase in the content of functional groups capable of reacting with active groups of lignin and cellulose. The probability of occurrence of such reactions is particularly high in surface layers under the conditions of film formation with a better efficient access of atmospheric oxygen.

By computer processing of the experimental results we obtained regression equations describing the effect of the main process parameters on the properties of the WFB specimens:

for the bending strength, MPa,

$$Y = 1.53 \times 10^{-5}(36.5 + 0.052a)$$
$$\times (40.5 - 0.0028b)(35.7 + 1.17c)(14.5 + 0.174d);$$

for the water absorption in 24 h, %,

$$Y' = 1.77 \times 10^{-4}(19.1 - 0.0173a)$$
$$\times (19.3 - 0.0236b)(18.0 - 0.065c)(19.6 - 0.0117d);$$

and for the swelling in thickness in 24 h, %,

$$Y'' = 4.87 \times 10^{-4}(14.4 - 0.022a)$$
$$\times (13.45 - 0.0116b)(13.14 - 0.11c)(15.85 - 0.021d).$$

These dependences are plotted in Fig. 2. They show that the following conditions ensure the best characteristics of the modified fiberboards: impregnation duration of 30 s, impregnating–formulation temperature of 100°C, heat treatment temperature of 180°C, and heat treatment duration of 7 h. However, the effect of the impregnation duration in the examined interval on the WFB properties is insignificant. This is caused by the fact that WFBs have low density, and the MA-modified copolymeric material readily penetrates into the WFB structure within a short

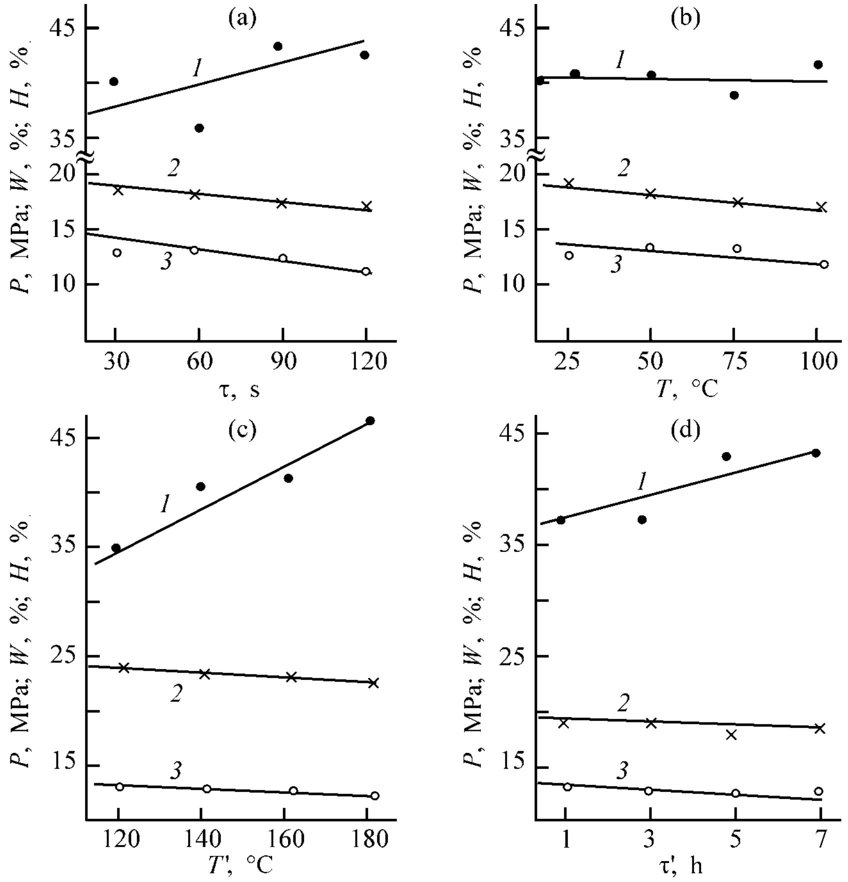


Fig. 2. Influence of (a) impregnation duration τ (30, 60, 90, 120 s; factor A), (b) impregnating formulation temperature T (25, 50, 75, 100°C; factor B), (c) heat treatment temperature T (120, 140, 160, 180°C; factor C), and (d) heat treatment duration τ (1, 3, 5, 7 h; factor D) on the parameters of WFB treated with the MA-modified polymeric material. (*1*) Water absorption W, (*2*) swelling in thickness H, and (*3*) bending strength P.

time. The effect of the impregnating–formulation temperature is also insignificant. To save power, it is advisable to perform the impregnation without heating. The strongest influence is exerted by the duration and especially by the heat treatment temperature, because cross-linking processes faster at elevated temperatures. Furthermore, at elevated temperatures maleic acid can undergo dehydration to maleic anhydride, and both can react with the wood components. Thus, elevated temperature and longer time of the heat treatment make possible the occurrence of a number of consecutive, parallel, and consecutive-parallel processes. The resulting 3*D* cross-linked copolymeric framework and its chemical bonding with the wood fiber impart to WFB not only increased hydrophobicity but also enhanced strength.

The content of the modified copolymeric material in the WFBs, influenced by the conditions of the impregnation and subsequent heat treatment, varied in a relatively narrow range, in most cases from 12 to 14.5% relative to the WFB weight.

Comparison of the experimental values with those calculated by the above-given regression equations for the corresponding conditions (Table 3) shows their good agreement.

The experimental results and the general physicomechanical and physicochemical concepts suggest the existence of an intimate correlation with a positive effect between the water absorption and swelling in thickness and between the water absorption and bending strength. These quantities are plotted in

Table 3. Experimental characteristics of WFB specimens treated with the MA-modified polymeric material

Parameter	Experiment	Calculation
Bending strength, MPa	44.8	47.1
Water absorption, %	15.9	17.1
Swelling in thickness, %	11.6	12.3

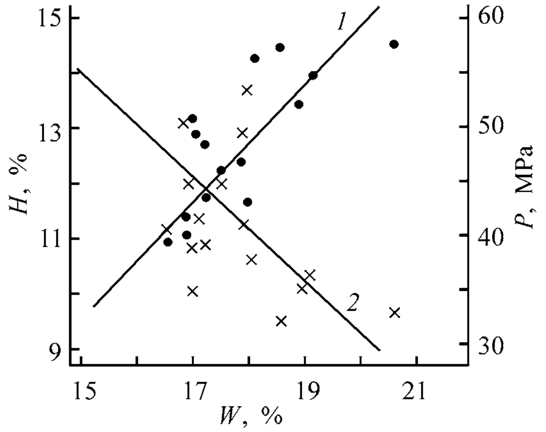


Fig. 3. (*1*) Swelling in thickness *H* and (*2*) bending strength *P* of WFB specimens as functions of the water absorption *W*.

Fig. 3; indeed, there is a positive correlation of the swelling in thickness and bending strength with the water absorption.

Visual examination of cuts of WFBs impregnated with the MA-modified copolymeric material shows that this material is uniformly distributed in the bulk of the fiberboard, filling the production defects and micro- and macropores. The resulting copolymeric framework of the MA-modified copolymeric material and products of its reaction with wood components reduces the release of formaldehyde from articles in which phenol– or urea–formaldehyde resins were used as binders.

The use of copolymeric materials prepared from petrochemical production wastes and by-products can not only improve of the properties of items but also solve environmental problems.

CONCLUSIONS

(1) Modification with maleic acid of a low-molecular-weight styrene-containing copolymer from by-product formed in polybutadiene production allows preparation of a material with an increased content of oxygen-containing functional groups.

(2) The copolymers modified with maleic acid can be used for protective treatment of wood materials with the aim to impart to them increased hydrophobicity and mechanical strength.

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