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Preparation and Use of Styrene-Containing Oligomer Treated by Pinane Hydroperoxide

O. N. CHERNYKH, I. N. PUGACHEVA and S. S. NIKULIN

Voronezh State University of Engineering Technologies,
Pr. Revolyutsii 19, Voronezh 394036 (Russia)

E-mail: assorty2009@yandex.ru

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Abstract

A high temperature process of treatment by pinane hydroperoxide was studied for styrene-containing oligomer obtained from polybutadiene by-products. It is demonstrated that the oxidized product obtained could be used for the production of emulsion rubber, as well as for the protective treatment of wood and wood-ware.

Key words: rubber, by-products, oligomers hydroperoxide, modification, emulsion, additive, wood protection

INTRODUCTION

Solving the problem of rational using the natural resources is inseparably linked with the processing and use of waste and by-products resulted from chemical and petrochemical plants. One of the most fast-growing industries today is presented by the production of synthetic rubber, monomers, solvents, wherein there is a large amount of different wastes (solid, liquid and gaseous) produced and accumulated. The processing and use of the latter represents an actual problem, which is faced not only by Russian, but also by all the developing countries.

The authors of [1, 2] demonstrated that on the basis of the waste by-products of petrochemical plants one could obtain low molecular copolymers with a high yield *via* the copolymerization between the by-products and styrene in the bulk or in the solution in the presence of ionic catalysts or radical initiators. At the same time, any attempts to synthesize copolymers from petrochemical by-products in the emulsion were unsuccessful. This could be caused by the fact that they contain compounds those either inhibit the copolymerization reaction or exhibit a low reactivity. The aqueous dispersions of polymers (emulsions) obtained from the wastes and by-products of petrochemical production, in some cases could be demanded in the industry [3]. For example, the process of obtaining an emulsion based on synthetic polyisoprene is implemented on an industrial scale. The possibility of obtaining and using the aqueous dispersions of polymers in industry was demonstrated by the authors of [4].

The approach proposed by the authors of [5, 6] has a major drawback: for dispersing, they used a hydrocarbon-based solution of a low molecular copolymer with the concentration amounting to 50–70 %. This could be caused by the fact that under normal conditions the low molecular mass copolymers obtained from petrochemical waste represent solid substances and transforming them into the liquid phase requires for using hydrocarbon solvents (toluene, xylene, nefras *etc.*). As the result, the process is complicated, the efficiency thereof is reduced, and moreover, a problem arises associated with trapping and processing these solvents. To reduce or to eliminate the use of a hydrocarbon solvent in the course of preparing of the aqueous polymer dispersion can be performed *via* reducing the polymer molecular mass and transferring them from the solid to the liquid, oily state. An example of such an approach can be presented by a thermo-oxidative effect on the polymers produced from the wastes and by-products of petrochemistry.

The purpose of this work consisted in studying the influence of thermal oxidation in the presence of pinane hydroperoxide upon changing the properties of a styrene-containing oligomer obtained from the by-products of polybutadiene manufacturing, as well as in studying the possibility of using the product obtained as an additive to emulsion rubbers and for the protective treatment of wood and products containing wooden components.

EXPERIMENTAL

At the first stage we determined the effect of a high-temperature impact of pinane hydroperoxide (PH) on a styrene-containing oligomer (SCO).

The thermal oxidation was performed as it follows. A reactor equipped with a stirrer was loaded with 100 g of an SCO solution in toluene (with the content of bound styrene amounting to about 80 % with the concentration of 70–75 %). Further, we added PH to the solution under constant stirring, and the reaction temperature was increased up to (100±2) °C. The pinane hydroperoxide was introduced in an amount of 1.0, 2.0, 3.0 mass % with respect to the initial amount of SCO. The total processing time was equal to 30 h, the process was monitored *via* periodic sampling from the reactor and the subsequent determination of the molecular mass by means of a viscometric method ($\overline{M_v}$), and of the acid number by means of an analytical method. Upon completion of the process, the solvent and other low boiling fractions were distilled from the resulting product. The molecular-mass characteristics of the original SCO and the SCO subjected to a high temperature treatment in the presence of PH (SCO PH) are presented in Table 1.

TABLE 1

Fractional distribution of macromolecules and their content in the SCO before and after thermal oxidation

$\overline{M_v} \cdot 10^{-3}$	Fraction content, %	
	before modification	after modification with PH
>300	0.11	0
200–300	0.19	0
100–200	0.64	0
50–100	1.57	0
20–50	4.33	0
10–20	4.92	0
5–10	4.18	0.08
3–5	13.00	1.17
1–3	31.33	20.08
0.5–1	28.96	59.26
<0.5	7.77	19.41

Note. According to the gel-penetration chromatography, for the initial SCO: $\overline{M_n} = 1200$, $\overline{M_w} = 6830$, $\overline{M_v} = 4420$, $\overline{M_z} = 84173$, $\overline{M_w} / \overline{M_n} = 5.68$, $\overline{M_z} / \overline{M_w} = 12.33$; for SCO after thermal oxidation with PH: $\overline{M_n} = 720$; $\overline{M_w} = 890$; $\overline{M_v} = 850$; $\overline{M_z} = 1260$; $\overline{M_w} / \overline{M_n} = 1.24$; $\overline{M_z} / \overline{M_w} = 1.42$, where $\overline{M_n}$ is the number-averaged molecular mass, $\overline{M_w}$ – is the mass-averaged molecular mass, $\overline{M_v}$ is the viscosity-averaged molecular mass, $\overline{M_z}$ is average molecular mass.

At the second stage of the work we investigated the possibility of obtaining a water–oligomer–antioxidant emulsion (WOAE) based on SCO, SCO PH and oil PN-6, as well as its influence upon the properties of the resulting rubber compounds and vulcanizates.

A stable emulsion was obtained in the presence of emulsifiers. For this, we introduced an antioxidant in SCO, PN-6 oil or SCO PH with further stirring at 50–60 °C for 0.5–2.0 h. Preliminary studies demonstrated that the use of PN-6 oil and unmodified SCO with no solvent for dispersing in an aqueous phase did not result in obtaining any stable emulsion, since the mentioned substances have a high viscosity. In order to obtain a stable emulsion, we added 20 % of solvent (toluene) to the PN-6 oil and unmodified SCO. Dispersing the SCO PH in an

TABLE 2

Properties of rubber mixture and vulcanizates based on rubber SKS-30 ARK

Parameters	SKS-30 ARK*	Oil PN-6	SCO	SCO-PH
Mooney viscosity (1 + 4 MB (100 °C)), a. u .:				
rubber	59.0	52.0	55.0	54.0
rubber mix	70.0	61.0	63.0	65.0
Mass fraction of antioxidant VTS-150, %	1.2	1.2	1.2	1.2
Mass fraction, %:				
free organic acids	5.6	5.8	6.2	6.3
soaps of organic acids	0.09	0.11	0.10	0.11
ash	0.21	0.20	0.19	0.22
Mass loss after drying (105 °C), %	0.18	0.19	0.21	0.24
Conditional stress at 300 % elongation, MPa	11.0	9.3	9.9	10.8
Conditional tensile strength, MPa	25.8	19.8	23.6	24.8
Relative elongation under breaking, %	630	660	610	680
Relative residual deformation, %	16	18	12	14
Rebound elasticity, %:				
at 20 °C	38	39	35	40
at 100 °C	48	48	50	46
Shore hardness *A*, a. u.	67	57	68	65
Coefficient of aging (100 °C, 72 h):				
according to conditional strength	0.60	0.61	0.68	0.70
according to conditional elongation	0.32	0.35	0.38	0.37

Note. Process conditions: vulcanization duration 60 min, temperature 143 °C; content PN-6 oil, SCO and SCO PH amounting to 3 mass %.

* Reference sample of the rubber mix and vulcanizate based on rubber SKS-30 ARK.

aqueous phase does not require any additional use of a hydrocarbon solvent, since the SCO PH represents an oily liquid with oxygen-containing functional groups those enhance the affinity thereof with respect to the aqueous phase.

Further, the stable WOAE prepared was mixed with rubber latex SKS-30 ARK. The resulting mixture was subjected to coagulation using a conventional procedure with using for this purpose the solutions of sodium and magnesium chloride, whereas as an acidifying agent we used an aqueous solution of sulphuric acid [7]. The water–oligomer–antioxidant emulsion was introduced into the butadiene-styrene rubber latex basing on a calculated SCO content in the rubber matrix equal to 2.0, 3.0, 4.0, 5.0, 6.0 mass %, whereas the antioxidants were added according to standard requirements.

Further, basing on the samples obtained, we prepared mixtures blends and investigated the physical and mechanical properties thereof. According to the properties the SCO PH is comparable with widely used industrial oil species, so we investigated the effect of SCO, SCO PH and oil PN-6 exerted on the parameters of rubber compounds and vulcanizates (Table 2).

At the third stage we studied the possibility of using the SCO PH for the protective treatment of wood and fibreboard (FB) using the plan of the Latin square of order 4 [8]. As the main factors which could determine the properties of wood and fibreboard, we choose the following ones: the temperature of the impregnating composition t_c = 60, 80, 100 and 120 °C (factor A), the heat treatment temperature (t_t) 70, 100, 130 and 160 °C (factor B), the duration of heat treatment (τ_t) 1, 3, 5 and 7 h (factor C). As the response functions we choose: water absorption (W, %), swelling in the tangential direction (P_t, %), swelling in the radial direction (P_r, %), thickness swelling (H, %), flexural strength (P, MPa).

The treatment of wood and fibreboard was performed as it follows. Weighed samples were immersed in an impregnating bath containing SCO PH with a siccative additive (about 10 %) to hold during 1 min for FB and during 1 h for wood. Choosing such a small time for fibreboard impregnation was caused by the fact that the FB has a lower density and so the impregnating material quickly and readily penetrates into the boards. Unlike the fibreboard the wood has a homogeneous structure and the penetration of low molecular mass SCO into the wood conductive elements those have small dimensions and contain water, is extremely difficult requiring for a long time.

For the processing we used the SCO that was obtained under the conditions providing both reducing the molecular mass of copolymers, and obtaining the products with a high content of functional groups (the processing time being equal to 17–20 h, the content of PH amounting to 3.0 mass %).

The additional introduction of a siccative promotes accelerating the processes of the formation of hydroperoxides and the decomposition thereof. The reactions involving atmospheric oxygen intensively occur in the surface layers. A limited access of oxygen into the bulk of the composition complicates the course of oxidative processes, and therein active high temperature polymerization reactions begin to activate involving various radicals occurring in the system ($R^\bullet$, $RO^\bullet$, $ROO^\bullet$). The process of film formation is inevitably accompanied by oxidative destruction, resulting in the formation of compounds containing the carbonyl, carboxyl, hydroxyl groups. This leads to further increasing the content of functional groups capable of reacting with the reactive groups of lignin and cellulose. The probability of such processes is especially high within the surface layers under the conditions of film formation with a good access of atmospheric oxygen [9].

The samples of wood material subjected to the treatment by SCO PH were taken from the bath, and then they were dried, thermally quenched and weighed. The content of SCO PH in the samples was determined gravimetrically according to increasing the mass.

RESULTS AND DISCUSSION

The high temperature treatment with SCO in the presence of PH within the first 15–18 h of the process leads to a decrease in the molecular mass of the resulting oligomer. This indicates an oxidative destruction process mainly occurs; thereby oxygen-containing functional groups are formed. The process of the destruction of the SCO polymeric chains could be presented as an oxidative destruction process concerning the units containing double bonds with the prevailing preservation of the styrene blocks [10, 11]. This is indicated by an increase in the acid number from 0.4–0.6 to 2.3–3.0 mg/g within the entire time interval. After passing about 15–18 h the system is characterized by minimal viscosity and molecular mass. Further, the viscosity of the system gradually increases due to increasing the molecular mass of the resulting products. This could be caused by the fact that at this stage the structuring processes prevail over the destruction processes in the system. Cross-linking the low molecular mass polymeric chains formed could be accompanied by the formation of oxygen-containing bridges. An additional introduction of PH has a positive impact on the course of the modification with SCO, which is indicated by a significant decrease in the molecular mass value (enhancing the destruction processes).

Thus, *via* varying the dosage of PH and duration of the process one could purposefully influence upon the properties of the resulting products. For example, when some specific cases require for the greatest level of reducing the molecular mass, the process is worthwhile to carry out at an increased content of PH (3.0 mass %) during 15–18 h. In the case when it is necessary to provide an increased content of oxygen-containing groups (increasing the polarity) with a higher molecular mass, the duration of the process is worthwhile to increase up to 30 h.

The analysis of the data presented in Table 1 shows that the resulting products exhibit an abrupt decrease in the content of high molecular fractions with increasing the proportion of low molecular fractions and with reducing the polydispersity level of the resulting low molecular mass polymers ($\overline{M_w}/\overline{M_n}$).

As noted earlier, the SCO obtained from petrochemical waste, can be used as filling agents in the emulsion polymerization of rubbers, in the tire and rubber industry, to enhance the hydrophobicity and durability of wood and wood-ware, wood-containing components. For this purpose, there was WOAE prepared on the basis of SCO, SCO PH and PN-6 oil. It is established that both sufficient uniformity and satisfactory delamination resistance are achieved when the content of the solution emulsifiers such as colophony soap or leukanol amounts to about 6 or 0.5 mass % per the amount of dispersed phase, respectively. Additionally using the WOAE allows improving the productivity of the process with achieving a uniform distribution of the filler in the bulk of rubber matrix.

We determined that the optimum content of SCO in the matrix of rubber SKS-30 ARK amounts to about 3.0 mass %. Increasing the SCO and the SCO PH content in the rubber matrix up to 5.0 mass % or more results in reducing the strength parameters of vulcanizates.

Testing the rubber mixtures and vulcanizates based on butadiene-styrene rubber SKS 30 ARK (see Table 2) demonstrated that the samples under testing, including SCO and SCO PH exhibit the best combination of properties in comparison with the sample treated with oil PN-6. Increasing the rate of aging for vulcanizates, to all appearance, could be caused by an effect of antioxidant encapsulation within the areas of microheterogeneous SCO concentration. An increased solubility of the amine-based and phenolic antioxidants in a low molecular mass and, consequently, a more polar oligomer comparing to the matrix of high molecular mass and weakly polar butadiene-styrene rubber leads to the fact that in the bulk of the rubber there are the stocking centers of formed. Those antioxidants, to all appearance, could be gradually released to migrate to the surface of the sample. This method of introducing the antioxidants results in increasing the resistance of rubber products with respect to thermal oxidation and thus belongs to a promising direction of efficient using the expensive antioxidants [12].

The interest in using the modified SCO for protective treatment of wood and fibreboard is based on the fact that the functional groups formed in the course of modification could react with the functional groups of wood components (cellulose, hemicellulose, and lignin) to form chemical bonds and hydrogen. This makes it possible to reduce the leachability of oligomeric impregnation composition from the product in the course of operation. The fact that of such an interaction is possible was demonstrated by the authors of [13], who used a low molecular mass copolymer on the base of distillation residues from styrene rectification and maleic anhydride as the impregnating material.

As the result of performing the high temperature treatment with SCO PH there occurs an abrupt decease in the proportion of high molecular mass fractions and an increase in the proportion of fractions with low molecular mass. Polymer molecules with low molecular mass are small, and therefore, they can easily penetrate into the conductive elements of the wood to bind with the material both due to chemical interaction, and owing to intermolecular forces.

The regression equations obtained according to the plan of a Latin square of order 4 those describe the influence of the main process parameters upon the properties of birchwood and FB samples, are as it follows:

1) for birch wood samples after 30 days after the test:

Water absorption, %:

$$W = 4.4 \cdot 10^{-4}(119.61 - 0.77t_c)(67.69 - 0.17t_t) \times (49.17 - 0.375\tau_t);$$

Swelling in the radial direction, %:

$$P_r = 1.84 \cdot 10^{-2}(9.56 - 0.024t_c)(8.86 - 0.013t_t) \times (7.56 - 0.045\tau_t);$$

Swelling in the tangential direction, %:

$$P_t = 1.04 \cdot 10^{-2}(14.04 - 0.046t_c)(12.29 - 0.021t_t) \times (10.81 - 0.24\tau_t)$$

2) for fibreboard samples:

Flexural strength, MPa:

$$F = 1.7 \cdot 10^{-3}(24.65 - 0.051t_c)(22.05 - 0.063t_t) \times (28.25 - 0.24\tau_t);$$

Water absorption (after 24 h), %

$$W = 1.46 \cdot 10^{-3}(26.64 - 0.0054t_c)(29.39 - 0.028t_t) \times (26.82 - 0.166\tau_t);$$

Thickness swelling (after 24 h), %

$$H = 2.3 \cdot 10^{-3}(23.58 - 0.0301t_c)(26.5 - 0.049t_t) \times (21.75 - 0.224\tau_t)$$

Basing on these data, graphs were plotted those demonstrate the influence of the mentioned factors upon the properties of birch-

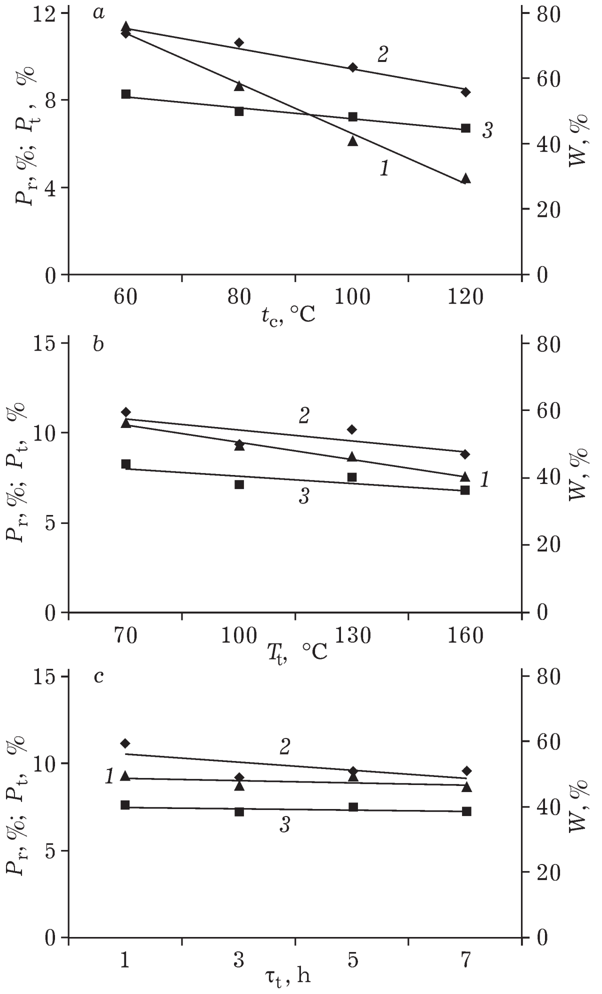

Fig. 1. Effect of composition temperature t_c (*a*), of the heat treatment temperature t_t (*b*) and the heat treatment duration τ_t (*c*) on the parameters of wood samples treated with SCO PH: *1* – water absorption (*W*); *2* and *3* – tangential swelling (P_t) and radial swelling (P_r), respectively.

wood and FB samples (Figs. 1 and 2, respectively).

Analyzing the dependences obtained, one could determine the optimum SCO PH processing conditions for wood samples:

1) the temperature of the SCO PH impregnating composition 120 °C, whereat the process of the protective treatment of wood could be carried out without solvent at elevated temperature;

2) heat treatment temperature amounting to 160 °C, which contributes to the acceleration of the spatial structuring of the polymeric matrix and allows reducing the duration of the process.

As the studies demonstrated, the duration of heat treatment (1–7 h) dos not significantly affect the properties of the resulting material.

In the case of FB it was found that the temperature of the composition and duration of heat treatment does not significantly affect the parameters of strength and hydrophobicity, since fibreboard represents a less dense material than wood. Owing to this, the SCO PH readily penetrates into the fibreboard; *i. e.* there is a process of FB impregnation occurs. The resulting polymer spatially structured skeleton imparts to the fibreboard not only increased hydrophobic properties, but also increased strength characteristics. The uniformity of coating and the completeness of impregnation is achieved at 60 °C during 1 min, whereas the recommended duration of thermal treatment amounts to 1 h.

The comparison of the calculated values obtained according to the above-listed equations with experimental data (Table 3) demonstrates a good agreement therebetween.

Basing on these results one could suggest that the content of SCO PH in the samples, water absorption, swelling and strength closely correlate with a positive effect (Figs. 3 and 4).

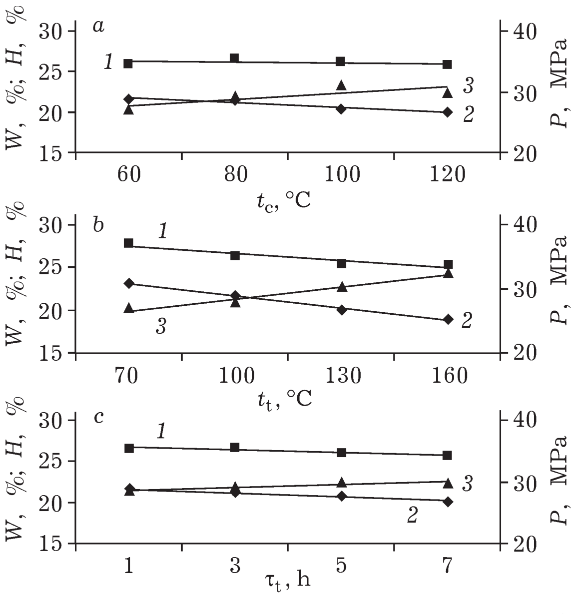

Fig. 2. Effect of composition temperature t_c (*a*), of the heat treatment temperature t_t (*b*) and the heat treatment duration τ_t (*c*) on the parameters of fibreboard treated by SCO PH: *1* – water absorption (*W*); *2* – thickness swelling (*H*); *3* – flexural strength (*P*).

TABLE 3

Comparison of calculated and experimental values for the parameters of the fibreboard and wood samples

Parameters	Calculation	Experiment
Fibreboard		
Water absorption, %	25.5	23.4 (30.5)
Thickness swelling, %	20.1	19.0 (27.6)
Flexural strength, MPa	29.7	27.8 (19.3)
Wood		
Water absorption, %	23.7	25.8 (130)
Swelling in the radial direction, %	6.3	5.9 (9.4)
Swelling in the tangential direction, %	8.4	7.6 (11.8)

Note. Parenthesized are the data for untreated samples after 30 days.

The sections of fibreboard treated with SCO PH clearly demonstrate that SCO PH is evenly distributed in the bulk of the resulting board to fill the manufacturing defects, as well as micro- and macro-pores. The resulting polymeric skeleton of spatially structured SCO and the products of its interaction with the wood components promotes reducing the formaldehyde emissions from the articles, wherein phenol-formaldehyde or urea-formaldehyde resins are used as binding agents.

The use of a modified oligomer as a treating composition for coating the wood and for the protective treatment of fibreboard samples allows one not only to improve the properties of the products, but also to solve environmental problems, in particular the problem of disposing the oligomers obtained from the waste and by-products of petrochemical industry. It should be noted that low-quality oligomers unsuitable for paint and varnish industry could be used for the mentioned purposes.

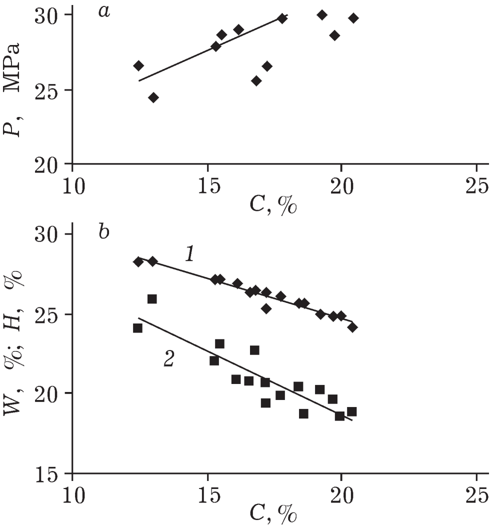

Fig. 3. Physical and mechanical properties of the fibreboard samples depending on the content of SCO PH (*C*): *a* – flexural strength (*P*); *b* – water absorption *W* (*1*) and the thickness swelling *H* (*2*).

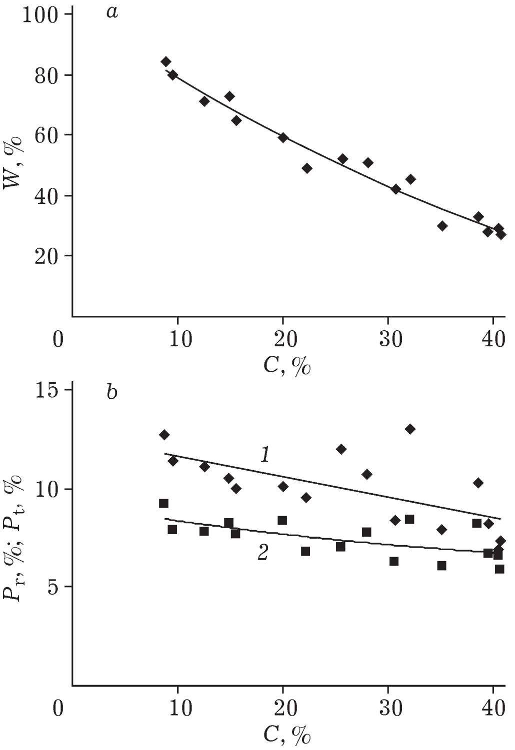

Fig. 4. Physical and mechanical properties of wood samples depending on the content of SCO PH (*C*): *a* – water absorption (*W*); *b* – tangential P_t (*1*) and radial swelling P_r (*2*).

CONCLUSION

1. It is established that the thermo-oxidative effect on the styrene-containing oligomer in the presence of pinane hydroperoxide allows one to purposefully modify the properties thereof, in particular the molecular mass and the content of oxygen-containing functional groups.

2. It is demonstrated that basing on a modified styrene-containing oligomer one can obtain a stable water–oligomer–antioxidant emulsion that hereinafter could find application in the production of emulsion rubber.

3. The introduction of water-oligomer antioxidant emulsion into rubber at the stage of obtaining thereof causes an increase in the resistance with respect to the thermo-oxidative effect of vulcanizates, offering the prospect of recycling large-scale wastes resulting from petrochemical production.

4. Using the modified styrene-containing oligomer for the protective treatment of natural wood and fibreboard provides enhancing the hydrophobic properties of the latter, whereas in the case of fibreboard there is enhancing of their strength characteristics observed.

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