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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Modification of Styrene-Containing Polymer with Pinane. Possible Applications of the Product

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Abstract—The influence of high-temperature treatment on the properties of a styrene-containing polymer prepared from by-products of polybutadiene production was studied. The use of the products in production of emulsion rubbers and for protecting treatment of wood materials was examined.

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Polymers prepared by emulsion (co)polymerization occupy a prominent place in world industry [1–4]. Emulsion polymerization does not require hazardous, inflammable, and explosive organic solvents and yields polymers with good physicomechanical properties. Studies are continued to improve the process for production of polymers by emulsion (co)polymerization and to extend the assortment of these polymers.

Polymers can be prepared in a high yield by (co)polymerization of wastes and by-products of petrochemical industry with styrene in a solution or in the bulk in the presence of both ionic and radical initiators [5, 6]. Hence, preparation of artificial aqueous dispersions of these polymers is promising. This procedure is based on fine mechanical dispersion of a polymer in an aqueous phase containing surfactants as stabilizers. Then the solvent is distilled off and the resulting dispersion is introduced into a latex. The possibility of such modification was demonstrated in [7, 8].

The substantial disadvantage of the process developed in our previous study [7, 8] is the use of a 50–70% hydrocarbon solution of the low-molecular weight polymer for preparing dispersions. In this case, an additional step, distillation of the hydrocarbon solvent from the aqueous polymer dispersion, is required. Since the polymers prepared from petrochemical wastes are solid under the ordinary conditions, a hydrocarbon solvent is required to prepare the aqueous polymer dispersion. Hydrocarbon solvents such as toluene, xylene, Nefras (commercial solvent based on butylbenzene), etc. are used to dissolve these polymers. This additional step complicates the process and decreases its efficiency. In addition, the problem of recovery and processing of these solvents arises. To eliminate the use of a hydrocarbon solvent or to decrease its content in an aqueous polymer dispersion, the molecular weight of the polymers should be decreased and solid polymers should be converted into an oil. For this purpose, the polymers prepared from wastes and by-products of petrochemical industry are subjected to thermal oxidative treatment.

It this study we examined the influence of thermal oxidative treatment in the presence of pinane hydroperoxide on the properties of a low-molecular-weight styrene-containing polymer prepared from polybutadiene production wastes. We also studied the possibility of using the product as an additive to emulsion rubber and for protecting treatment of wood materials.

EXPERIMENTAL

First we determined the molecular weight of styrene-containing low-molecular weight polymer (SLMWP) treated at 100 ± 2°C in the presence of pinane hydroperoxide (PH). The thermal oxidative treatment was performed by the following procedure.

A reactor equipped with a stirrer was charged with 100 g of a toluene solution of SLMWP containing 70–75 wt % of bound styrene. PH in amount of 0, 1.0, 2.0, and 3.0 wt % of the initial SLMWP was added to the solution with continuous stirring. The reaction mixture was heated to 100 ± 2°C. The total time of the process was 30 h. Samples of the reaction mixture were taken at regular intervals, their molecular weight $\overline{M}_v$ was measured viscometrically, and the acid number was determined analytically. After treatment completion, the solvent and other low-boiling fractions were distilled off from the product.

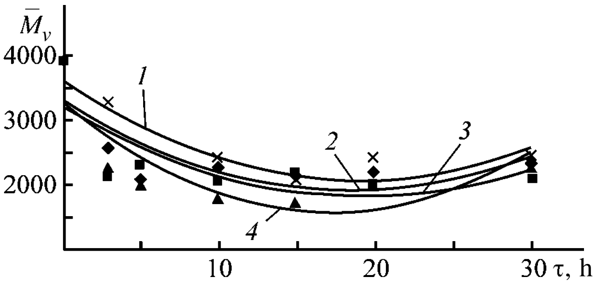

Fig. 1. Molecular weight $\bar{M}_v$ of SLMWP as a function of the time of thermal oxidative treatment τ. (*1*) Without PH and with (*2*) 1.0, (*3*) 2.0, and (*4*) 3.0 wt % of PH; the same for Fig. 2.

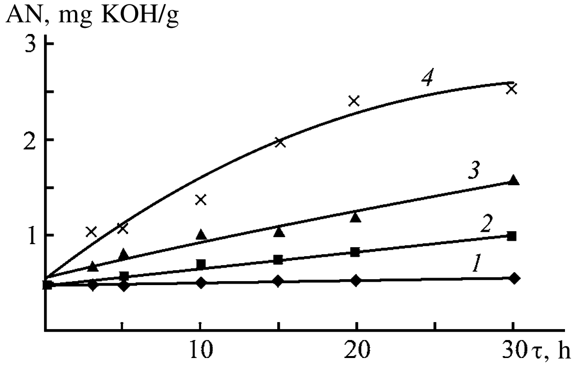

Fig. 2. Acid number AN as a function of the time of thermal oxidative treatment τ.

The molecular weight of the polymer decreases after the high-temperature (100°C) treatment of SLMWP in the presence of PH within the first 15–18 h (Fig. 1). This fact suggests that the thermal treatment involves mainly oxidative degradation to form products with oxygen-containing functional groups.

Table 1. Molecular weight and content of SLMWP fractions before and after thermal oxidativer treatment*

$\bar{M}_w \times 10^{-3}$	Content of fractions, %	
	initial SLMWP	modified SLMWP
>300	0.11	–
200–300	0.19	–
100–200	0.64	–
50–100	1.57	–
20–50	4.33	–
10–20	4.92	–
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

* According to the results of gel-permeation chromatography, SLMWP has the following molecular-weight parameters: initial, $\bar{M}_n = 1200$, $\bar{M}_w = 6830$, $\bar{M}_v = 4420$, $\bar{M}_z = 84\,173$, $\bar{M}_w/\bar{M}_n = 5.68$, $\bar{M}_z/\bar{M}_w = 12.33$; modified, $\bar{M}_n = 720$, $\bar{M}_w = 890$, $\bar{M}_v = 850$, $\bar{M}_z = 1260$, $\bar{M}_w/\bar{M}_n = 1.24$, $\bar{M}_z/\bar{M}_w = 1.42$.

Degradation of SLMWP macromolecules can be considered as oxidative degradation of the units containing double bonds with preservation of styrene blocks [9, 10].

An increase in the acid number from 0.4–0.6 to 2.3–3.0 mg KOH/g in the whole temperature range (Fig. 2) confirms this assumption. The minimal viscosity and molecular weight are attained in 15–18 h. Then the viscosity and molecular weight of the system gradually increase, which can be due to prevalence of the cross-linking over degradation.

Low-molecular-weight polymers can cross-link to form oxygen-containing bridges.

Introduction of an additional amount of pinane hydroperoxide has a positive effect on the SLMWP modification: the molecular weight decreases to a greater extent (intensification of degradation) and the acid number increases.

Thus, our experimental data show that the properties of the products of thermal oxidative degradation can be controlled by the amount of PH added and the treatment duration. Polymers with minimal molecular weight can be prepared by treatment in the presence of 3.0 wt % PH for 15–18 h. To obtain polymers with an increased content of oxygen-containing groups (increased polarity) and a higher molecular weight, longer treatment (30 h) is required.

The molecular-weight characteristics of the initial and modified SLMWP are presented in Table 1.

As seen from Table 1, the content of high-molecular-weight fraction sharply decreases, the content of the low-molecular-weight fraction increases, and the polydispersity ($\bar{M}_w/\bar{M}_n$) decreases.

As shown above, polymers prepared from petrochemical wastes can be used as fillers of emulsion polymerization rubbers, in tire and industrial rubber production, and as agents increasing the hydrophobicity and strength of wood and wood-containing articles. We tested for these applicxation SLMWP treated at high temperature in the presence of PH. We also examined the influence of the modified SLMWP on the properties of rubber, rubber stocks, vulcanizates, and wood fiberboards (WFB).

First we prepared an aqueous oligomer–antioxidant emulsion (AOAE) of modified SLMWP. A stable emulsion was obtained in the presence of emulsifiers on a unit equipped with a high-speed stirrer. An antioxidant was added to a toluene solution of modified

SLMWP and PN-6 oil (petroleum oil containing up to 14 wt % paraffin–naphthene hydrocarbons and up to 19 wt % light and up to 65 wt % medium aromatic hydrocarbons; this oil is widely used in production of extended rubbers). The mixture was stirred at 50–60°C for 0.5–2.0 h. Our preliminary results showed that no stable aqueous emulsion was formed in the presence of PN-6 oil and unmodified SLMWP without a solvent. Since these products are highly viscous, special equipment should be used for dispersing them. To prepare a stable emulsion, 20% of a solvent (toluene) was added to unmodified SLMWP and NP-6 oil.

An aqueous dispersion of SLMWP modified with PH can be prepared without introduction of a hydrocarbon solvent, since the products are oily liquids whose molecules have hydrophilic oxygen-containing functional groups.

Since the oxidative treatment of SLMWP with PH is performed in toluene, antioxidants used in production of emulsion rubber should be dissolved in an oxidized SLMWP solution prior to distillation of the solvent and low-molecular-weight products. As a result, the antioxidant will be uniformly distributed an SLMWP. Then, the solution of oxidized SLMWP and an antioxidant was emulsified and the low-molecular fraction was distilled off.

We found that the fairly uniform emulsion satisfactorily stable to phase separation can be prepared at the emulsifier content (rosin soap) of approximately 6.0 wt % and Leukanol content of 0.5 wt % relative to the dispersed phase. The content of the dispersed phase after distillation of the low-boiling fraction was 35–40 wt %.

The stable AOAE was mixed with SKS-30 ARK rubber latex and the resulting mixture was coagulated by the conventional procedure using a sodium chloride solution as a coagulating agent and a sulfuric acid solution as an acidifier [11]. The polymer content in the rubber matrix was 2.0, 3.0, 4.0, 5.0, and 6.0 wt % of the rubber and the antioxidant content was 1.2 wt % of the rubber.

Our results showed that introduction of AOAE increases the productivity of the process and results in uniform distribution of the filler in the bulk of the rubber matrix.

We prepared rubber stocks containing SLMWP samples and studied their physicomechanical properties. The optimal content of modified SLMWP in the matrix of SKS-30 ARK rubber is approximately 3.0 wt %. The strength of the vulcanizates decreases by 20–30% at the content of modified SLMWP in the rubber matrix increased to 5.0 wt %. The use of this rubber in critical articles is undesirable. However, rubber stocks with high SLMWP content can be used for preparing less critical articles such as rugs etc.

Modified SLMWP is an oily liquid whose properties are close to those of common widely used industrial oils. We performed a comparative study of the influence of SLMWP, SLMWP subjected to thermal oxidative degradation, and PN-6 oil on the properties of the rubber stocks and vulcanizates (Table 2).

Our tests of rubber stocks and vulcanizates prepared from SKS-30 ARK butadiene–styrene rubber showed that the properties of the samples containing initial and oxidized SLMWP were better than those of the samples containing PN-6 oil.

Among the positive properties of the composites are deceleration of a decrease in their strength with time, which is due to more uniform distribution of the antioxidant in the rubber matrix. In addition, the thermal resistance of the composite is enhanced.

An increase in the thermal aging coefficient is probably caused by encapsulation of the antioxidant in the areas on microheterogeneous concentration of the modified polymer. This is due to the fact that the solubility of amine and phenolic antioxidants in low-molecular-weight and more polar oxidized SLMWP is higher than that in the matrix of high-molecular-weight and low-polarity butadiene–styrene rubber. As a result, sites with high antioxidant concentrations appear in the bulk of the rubber. The concentration of the antioxidant in these sites decreases during their migration to the sample surface. Thus, this procedure for introducing antioxidants enhances the resistance of rubber articles to thermal oxidative aging and is an example of the efficient use of expensive antioxidants [12].

The next step of this study was to impregnate wood fiberboards (WFBs) with oxidized SLMWP.

The use of SLMWP treated with PH for this purpose is based on the assumption than the functional groups formed in the course of oxidation can react with the functional groups of wood components (cellulose, hemicellulose, and lignin) to form both chemical and hydrogen bonds. Formation of these bonds decreases the washout of a coating from an article in the course of its operation. The possibility of this interaction was demonstrated in our previous study [13] where a low-molecular-weight copolymer of the bottoms from styrene distillation and maleic anhydride was used for impregnation.

Table 2. Properties of rubber stocks and vulcanizates prepared from SKS-30 ARK rubber. Vulcanization time 60 min; temperature 143°C; the content of PN-6 oil and of initial and oxidized SLMWP 3.0 wt %

Property	SKS-30 ARK (reference*)	NP-6 oil	Initial SLMWP	Oxidized SLMWP
Mooney viscosity [MB 1 + 4 (100 OS)], arb. units:				
rubber	59.0	52.0	55.0	54.0
rubber stock	70.0	61.0	63.0	65.0
Weight fraction of VTS-150 antioxidant, %	1.2	1.2	1.2	1.2
Weight fraction, %:				
free organic acids	5.6	5.8	6.2	6.3
soap of organic acids	0.09	0.11	0.10	0.11
ash	0.21	0.20	0.19	0.22
Weight loss after drying at 105°C, %	0.18	0.19	0.21	0.24
Nominal stress at 300% elongation, MPa	11.0	9.3	9.9	10.8
Nominal tensile strength, MPa	25.8	19.8	23.6	24.8
Relative elongation at break, %	630	660	610	680
Elongation set, %	16	18	12	14
Rebound elasticity, %:				
20°C	38	39	35	40
100°C	48	48	50	46
Shore hardness *A*, arb. units	67	57	68	65
Thermal resistance with respect to:				
nominal tensile strength, MPa	7.8	7.9	11.1	8.9
relative elongation at break, %	120	160	180	290
Aging coefficient (100°C, 72 h) with respect to:				
nominal strength	0.60	0.61	0.68	0.70
relative elongation	0.32	0.35	0.38	0.37

* Reference sample of rubber stock and vulcanizate prepared from SKS-30 ARK rubber.

High-temperature treatment with PH of styrene-containing SLMWP prepared from polybutadiene production wastes sharply decreases the content of high-molecular-weight fractions and increases the content of low-molecular-weight fractions (Table 1). It should be noted that SLMWP penetrates in conductive elements of wood and gets bound with them in the course of the treatment of wood-containing materials.

The treatment was performed as follows. The WFB samples were weighed, immersed in an impregnation bath containing SLMWP subjected to thermal oxidative treatment in the presence of ~10% dryer, and kept for 1 min. Impregnation was performed at 60°C with subsequent heating at 160°C for 3 h. We chose these conditions on the basis of the known procedure for protecting treatment of wood materials by polymers prepared from petrochemical by-products [13, 14]. For impregnation we used SLMWP heated at 100°C for 17–20 h in the presence of 3.0 wt % PH.

Introduction of dryer accelerates both formation and decomposition of hydroperoxides. Intense reactions with atmospheric oxygen occur in the surface layers. In the depth of the composite, the contribution of the oxidation processes decreases owing to restricted oxygen access, and the contribution of high-temperature polymerization increases. These reactions are activated by various radicals present in the system.

Formation of films is inevitably accompanied by oxidative degradation to form compounds with carbonyl, carboxy, and hydroxy groups. The number of functional groups capable of interacting with reactive groups of lignin and cellulose increases. The probability of these processes is particularly high in the surface layers under conditions of film formation on exposure to air.

Our experimental results show that the treatment enhanced the stability of the WFB shape, its resistance to water and high humidity, and the mechanical properties (Table 3). Visual inspection of WFB sections showed a uniform distribution of oxidized SLMWP in the bulk of the board and filling of manufacturing

Table 3. Experimental properties of WFB samples treated with oxidized SLMWP

Property	Experiment	Reference*
Bending strength, MPa	25.6	17.8
Water absorption, %	23.9	36.5
Swelling in the thickness, %	17.1	25.7

* Reference WFB samples without treatment.

defects and of micro- and macropores. The polymer framework formed from three-dimensionally cross-linked styrene-containing SLMWP and the products of its reaction with wood components decreases the formaldehyde release from the articles prepared using phenol– or urea–formaldehyde resins as the binder.

Protective treatment of wood materials with SLMWP prepared from by-products and wastes from petrochemical industry not only improves their properties but also solves environmental problems.

CONCLUSION

High-temperature treatment of low-molecular-weight styrene-containing copolymer prepared from by-products of polybutadiene production decreases the molecular weight of the polymer and increases the content of oxygen-containing functional groups. The modified polymer can be used in production of extended rubbers and for protective treatment of wood materials.

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