

Wood Flour: A New Filler for the Rubber Processing Industry. III. Cure Characteristics and Mechanical Properties of Nitrile Butadiene Rubber Compounds Filled by Wood Flour in the Presence of Phenol-Formaldehyde Resin

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ABSTRACT: Nonmodified and corona-activated conifer wood flour was evaluated as filler to nitrile butadiene rubber (NBR) compounds containing different amounts of phenol-formaldehyde resin (PFAR) by studying the cure characteristics and the mechanical properties of the filled compounds. It was found that the PFAR affects considerably the cure characteristics and the mechanical properties of the wood flour-filled NBR compounds due to a presumable action as an interface interactions modifier. Acting as an antiaging agent it improves also their thermal-oxidative stability. The optimal amount of PFAR regarding the cure characteristics and mechanical parameters is of 15 phr/100 phr wood flour. The addition of PFAR just before the wood flour is preferable because of both its better homogenization

in the rubber matrix and its lower adsorption by the wood flour, leading to an improvement of the mechanical properties of the wood flour-filled NBR compounds. The replacement of nonmodified wood flour by corona-activated wood flour leads to additional increase of the mechanical parameters without significant affect of the optimum cure time, aging resistance, and water adsorption. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 95–101, 2004

Key words: nonmodified and corona activated conifer wood flour; filled NBR compounds containing phenol-formaldehyde resin; cure characteristics; mechanical properties; aging resistance; water adsorption

INTRODUCTION

In a former study¹ we found that the wood flour acts as nonreinforcing filler in nitrile butadiene rubber (NBR) compounds. Scanty information about wood flour modification directed to its application as an active filler in polymer composites or rubber compounds could be found in the technical literature. Marcovich et al.² have esterified wood flour and have used it as a thermosetting filler to unsaturated polyester-styrene resins. Alma and Shirashi³ have phenolated (in presence of sulfuric acid as a catalyst) birch wood flour and have tested the obtained phenolated wood resin as a thermosetting material.

During the last decade, there has been increasing interest in the use of suitable interface interactions modifiers to increase the interface adhesion, to control the morphology of the composites, and to obtain materials with desirable properties⁴. Long ago, the reinforcing effect of the phenol-formaldehyde (PFAR) res-

ins combined with hexamethylenetetramine in NBR compounds, as well as their participation in the rubber vulcanization process are known^{5–7}. On the other hand, it is also known that these resins are able to interact with the wood flour and, acting as an interface interactions modifier, to improve the wood flour/polymer matrix interface interaction in the wood flour-filled polymers such as PVC.^{8–10} We present here how the cure characteristics and some mechanical properties of NBR compounds filled by nonmodified or corona-treated wood flour are affected by the presence of PFAR as an interface interaction modifier.

EXPERIMENTAL

Nitrile butadiene rubber (NBR 40, manufactured in Russia, with parameters according to Russian standard GOST 7738–79) and conifer wood flour (Maritsa, Kostenets, Bulgaria; manufactured with parameters according to Bulgarian standard BDS 3781–74, particle size of 100–140 μ m, and humidity of 6%) were used in this study.

The PFAR was novolac resin (P. Volov, Bulgaria) manufactured with parameters according to Bulgarian standard BDS 10–80.

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TABLE I
Wood Flour-Filled NBR Compounds, Containing PFAR Added Together with (Mixtures 2–16)
or Just Before (mixtures 7'–11') this Wood Flour

Mixture No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
							7'	8'	9'	10'	11'					
Wood Flour (phr)	0	20	35	50	70	90	20	35	50	75	90	20	35	50	70	90
PFAR (phr)*	0	10	10	10	10	10	15	15	15	15	15	20	20	20	20	20

* Per 100 phr wood flour; PFAR contains 5 phr hexamethylenetetramine, added just before mixing on the rolls.

The model NBR compounds contain traditional ingredients (phr): NBR 40, 100; wood flour (nontreated or corona treated), varied; PFAR, varied; stearic acid, 2; zinc oxide, 3; sulfur, 2; and sulfenamide accelerator (Vulkacit CZ, Byer), 2. The variables, wood flour, and PFAR amounts are shown in Table I. All the materials used were of standard rubber industry grade and were not purified for this study.

The modified wood flour was prepared by corona treatment in air, as described in Vladkova et al.¹¹ under the following conditions: thickness of the wood flour layer, 4 mm; voltage, 12 kV; and duration of treatment, 10 min.

The model mixtures were prepared on laboratory roll with a friction ratio of 1 : 1.4. The premixing of the wood flour with the PFAR was difficult due to the high viscosity of the resin. To avoid the use of extender we added the PFAR (with 5 phr hexamethylenetetramine/100 phr PFAR added to the resin just before use) directly to the rubber mixture together with the wood flour or just before it.

The vulcanization characteristics were determined according to Bulgarian standard 15,754–83 with a Monsanto Rheometer M100 at a temperature of 170°C. The vulcanization was carried out at this same temperature and the optimum cure time.

The mechanical parameters were determined according to ISO/R37 and the heat aging was according to ISO/188.

The water adsorption was measured using 50 × 50 × 2 mm samples kept in distilled water for 24 h. The corresponding calculations were performed with the following formula:

$$Wa = (P_1 - P_0) \times 100/P_0\%$$

where Wa is the water adsorption; P_0 is the weight of the sample before testing; and P_1 is the weight of the sample after keeping in water.

The microscope photographs are taken from nonvulcanized samples in polarized light using a MBI-6 microscope.

RESULTS AND DISCUSSION

We studied earlier the effect of nonmodified¹ as well as of corona-treated conifer wood flour¹¹ as a filler to

NBR compounds in the absence of any interface interactions modifier. This study was aimed to evaluate PFAR as an interface interactions modifier, therefore, our experiments were carried out in three sets:

Set 1 (Table I, mixtures 2–16) studied the influence of different amounts PFAR: 10 phr (Table I, mixtures 2–6), 15 phr (Table I, mixtures 7–11), or 20 phr (Table I, mixtures 12–14) present in the corresponding NBR compounds, filled by 10–90 phr wood flour.

Set 2 (Table I, mixtures 7–11 and 7'–11') studied the effect of the manner of PFAR compounding in the wood flour-filled NBR compounds on the cure characteristics and mechanical properties of the corresponding composites. Therefore we carried out comparative testing of a number of wood flour-filled NBR compounds containing equal amounts PFAR (15 phr/100 phr WF) added together with the wood flour (Table I, mixtures 7–11) or just before it (Table I, mixtures 7'–11').

Set 3 was aimed at the evaluation of the effect of corona-activated wood flour in the presence of PFAR. Therefore we performed comparative experiments with two series of NBR compounds containing equal amounts PFAR added in the same manner (just before the wood flour) but filled by nonmodified (Table I, mixtures 7'–11') or corona-activated conifer wood flour (Table II, mixtures 7'–11').

Cure characteristics

The cure characteristics of the wood flour-filled NBR compounds in the presence of different amounts (10, 20, or 30 phr/100 phr WF) PFAR (containing 5 phr hexamethylene-tetramine/100 phr resin) are presented in Figure 1. It is evident that all wood-filled compounds have slight higher M_{\min} (curves 1–3) compared to nonfilled compounds, as expected. But the comparison of curves 1–3 shows that M_{\min} decreases

TABLE II
NBR Compounds Containing 15 phr PFAR Added Just Before the Corona-Treated Wood Flour

Mixture No.	7''	8''	9''	10''	11''
CTWF (phr)	20	35	50	70	90

CTWF, corona-treated wood flour.

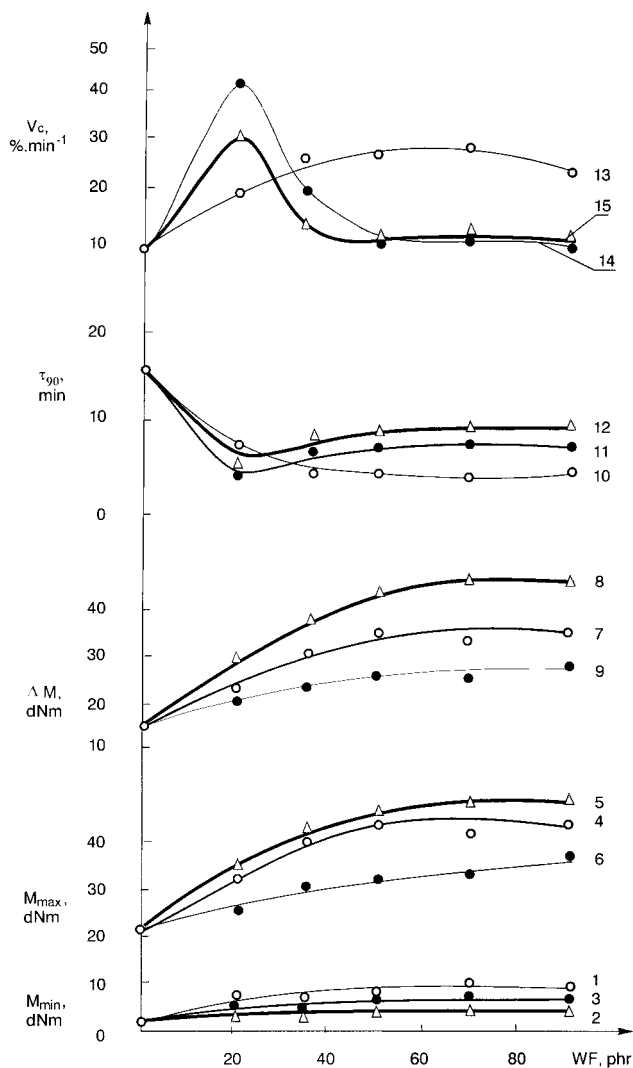


Figure 1 Cure characteristics: M_{\min} (curves 1–3), M_{\max} (curves 4–6), ΔM (curves 7–9), τ_{90} (curves 10–12), and cure rate, V_c (curves 13–15) of wood flour-filled NBR compounds, containing different amounts PFAR (with 5 phr hexamethylenetetramine/100 phr resin). 10 phr: curves 1, 4, 7, 10, and 13; 15 phr: curves 2, 5, 8, 11, and 14; and 20 phr: curves 3, 6, 9, 12, and 15 phr.

slightly with increase of PFAR amount from 10 up to 15 phr at all levels of filling by wood flour. This could be due to some plasticizing effect of the PFAR. As was expected⁶, no significant changes were observed in the scorch time, τ_{s1} . In all cases it was about 3–4 min and therefore any curves are presented in the figure. A comparison of the next two groups of curves in Figure 1 (curves 4–6 and curves 7–9) shows the differences in the M_{\max} and ΔM , respectively, when different PFAR amounts (10, 15, or 20 phr) were present in the studied compounds. The highest values of M_{\max} and ΔM are present in the mixtures containing 15 phr resin at any wood flour filling level. The optimum cure time, τ_{90} (compare curves 10–12), and the cure rate, V_c (compare curves 13–15), of the wood flour-filled NBR com-

pounds depend also on the amount of the PFAR present in the mixture. The differences observed in the cure characteristics: optimum cure time, τ_{90} , M_{\min} , M_{\max} , and ΔM of the wood flour-filled NBR compounds, containing different PFAR amounts could be accepted as an indication for the existence of significant differences in the rubber matrix/wood flour interface interaction¹².

The results of our comparative testing of a number of wood flour-filled NBR compounds containing equal amount PFAR (15 phr/100 phr WF) added together with the wood flour (Table I, mixtures 7–11) or just before it (Table I, mixtures 7'–11') are presented in Figure 2. The comparison of curves 1 and 2 shows that M_{\min} does not change significantly; curves 4 and 5 as well as 7 and 8 show that M_{\max} and ΔM , respectively, increase; the optimum cure time, τ_{90} (curves 10 and 11) decreases, and the cure rate, V_c (compare curves 13 and 14) increases slightly (excluding the filling levels under 35 phr where the changes are opposed). All differences observed in the cure characteristics of the mixtures containing equal PFAR amounts added together with the wood flour or just before it indicate probable different dispersion of the resin in the rubber matrix as well as in the wood flour in both cases. This reflects on the cure processes and affects the vulcanization parameters.

Expecting higher activity of the corona-treated wood flour as a filler to NBR compounds containing PFAR, as was found for similar NBR compounds but not containing this resin¹⁰, we made a third set of experiments at which the nonmodified conifer wood flour was replaced by a corona treated one. The results of the comparative study of the cure characteristics of NBR compounds containing 15 phr PFAR, added just before the filler and filled by nonmodified or corona-treated wood flour, are presented in Figure 2. It is evident that the use of corona-activated instead of nontreated wood flour leads to an increase in M_{\min} (compare curves 2 and 3 in Fig. 2), M_{\max} (compare curves 5 and 6 in Fig. 2), and ΔM (compare curves 8 and 9) when the filling level is under 35 phr. The optimum cure time, τ_{90} (compare curves 11 and 12 in Fig. 2), and the cure rate, V_c (compare curves 14 and 15 in Fig. 2), are almost equal for the mixtures filled by nonmodified or corona-treated wood flour.

Evidently, the replacement of nonmodified wood flour by corona treated wood flour leads to more pronounced changes in the cure characteristics of the filled NBR compounds containing PFAR compared to similar compounds that do not contain this resin¹¹.

Mechanical properties, water adsorption, and aging

The results of a comparative mechanical testing of wood flour-filled NBR vulcanisates in the presence of different PFAR amounts are presented in Figure 3. It is

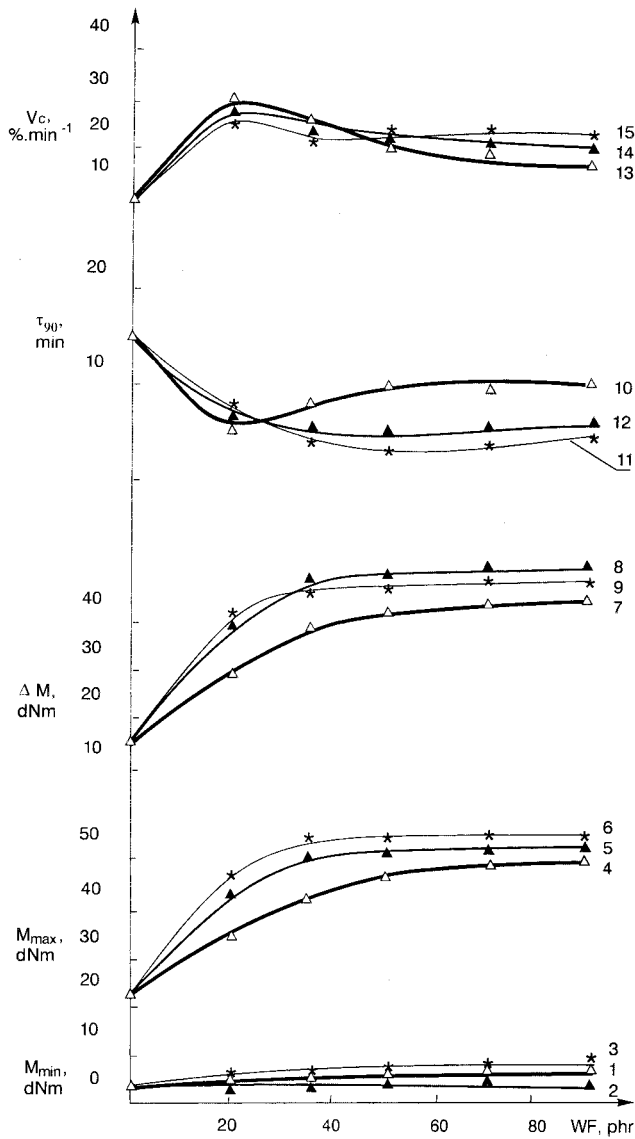


Figure 2 Cure characteristics: M_{\min} (curves 1–3), M_{\max} (curves 4–6), ΔM (curves 7–9), τ_{90} (curves 10–12), and cure rate, V_c (curves 13–15) of wood flour-filled NBR compounds, containing 15 phr PFAR (with 5 phr hexamethylenetetramine/100 phr resin), added together with conifer wood flour (curves 1, 4, 7, 10 and 13) or just before it (curves 2, 5, 8, 11 and 14). Curves 3, 6, 9, 12, and 15 correspond to NBR compounds containing the same amount (15 phr) of PFAR, added just before the filler, but the nonmodified wood flour was replaced by corona-activated wood flour.

evident that all wood flour-filled NBR vulcanisates containing PFAR (10, 15, or 20 phr) have increased modulus M_{100} (Fig. 3, curves 1–3) and Shore A hardness (Fig. 3, curves 10–12) compared to the control nonfilled compound and as it is in the absence of PFAR (Fig. 3, curve 1'). Both parameters, the modulus M_{100} and Shore A hardness, increase with the increase of the filling level, as in the absence of PFAR (Fig. 3, curve 10'). The elongation at break, ϵ (Fig. 3, curves 7–9), decreases with the increase of the filling level,

excluding the vulcanisates containing 15 or 20 phr PFAR/100 phr wood flour and wood flour up to 35 phr/100 phr rubber. A slight increase in this parameter is observed in the range of the relatively low filling level (about 20–35 phr wood flour). Contrary to the NBR compounds filled by wood flour in absence of PFAR, at which the tensile strength, σ (Fig. 3, curve

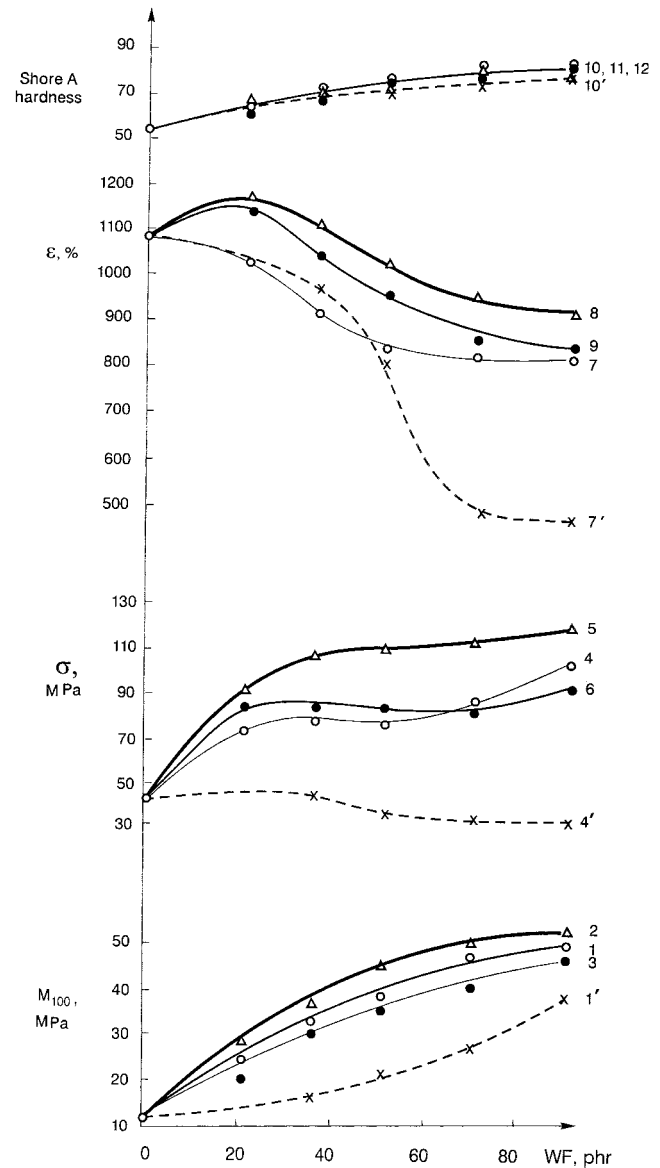


Figure 3 Mechanical parameters: modulus, M_{100} (curves 1–3), tensile strength, σ (curves 4–6), elongation at break, ϵ (curves 7–9), and Shore A hardness (curves 10–12) of wood flour-filled NBR compounds, containing 15 phr PFAR (with 5 phr hexamethylenetetramine/100 phr resin), added together with conifer wood flour (curves 1, 4, 7, 10, and 13) or just before it (curves 2, 5, 8, 11, and 14). For comparison, curves 1', 4', 7', and 10' corresponding to NBR compounds filled by wood flour in the absence of PFAR are presented here. Curves 3, 6, 9, 12, and 15 correspond to NBR compounds containing the same amount (15 phr) of PFAR, added just before the filler, and corona-activated instead of nonmodified wood flour.

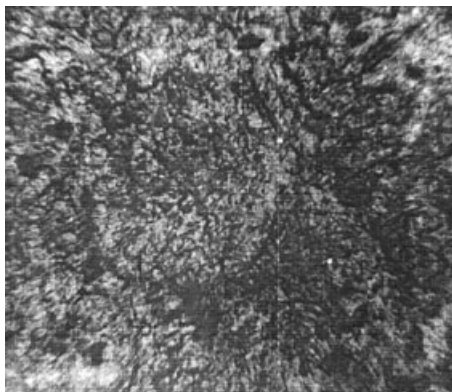


Figure 4 General picture of the wood flour dispersion in the polymer matrix ($\times 50$). NBR filled by 50 phr conifer wood flour in the presence of 15 phr PFAR/100 phr wood flour. All other samples are similar and therefore their photographs are not presented here

4'), demonstrates a tendency to slightly decrease with the increase of the filling level, the tensile strength, σ , of the NBR vulcanisates containing PFAR (Fig. 3, curves 4–6) increases with the increase of the filling level. The differences observed in the mechanical parameters of the vulcanisates containing or not containing PFAR indicate the existence of some differences in the interface interactions in the presence and absence of PFAR. The comparison of the groups of curves 1–3, 4–6, and 7–9 in Figure 3 shows that the modulus, M_{100} ; the tensile strength, σ ; and the elongation at break, ε , respectively, of the wood flour-filled NBR compounds at all filling levels depend significantly on the amount (10, 15, or 20 phr) of the PFAR. These parameters (excluding the elongation at break ε that have maximal values at 20 phr PFAR) have maximal values at 15 phr PFAR. The increase of the M_{100} is up to over five times (it is up to about 3.5 times in absence of PFAR) and of the tensile strength is up to about 2.4 times (there is slight decrease in absence of PFAR) at 90 phr wood flour in presence of 15 phr PFAR. The different amounts of PFAR present in the wood flour-filled NBR compounds does not affect significantly the Shore A hardness (compare curves 10–12 in Fig. 3). The changes observed in the other mechanical parameters, M_{100} and tensile strength of the wood flour-filled NBR compounds in the presence of different PFAR amounts, are in compliance with the changes observed in M_{\max} and ΔM from the Monsanto rheograms (see Fig. 1, curves 4–6 and 7–9). Any clearly expressed anisotropy is observed in the PFAR-containing NBR compounds filled by wood flour as demonstrated our microscopy study (Fig. 4).

The mechanical parameters of the wood flour-filled NBR compounds containing equal amounts (15 phr) of PFAR added together with the wood flour (curves 1, 4, 7, 10, and 13) or just before it (curves 2, 5, 8, 11,

and 14) are presented in Figure 5. The addition of the PFAR just before the wood flour leads to additional increase of the modulus, M_{100} (compare curves 1 and 2 in Fig. 5), tensile strength, σ (compare curves 4 and 5 in Fig. 5), and the elongation at break, ε (compare curves 7 and 8 in Fig. 5), which could be due to better homogenization of the PFAR in the rubber matrix as well as of some affect of the cure process. This last one is confirmed by all changes observed in the cure parameters (see Fig. 2). The Shore A hardness (compare

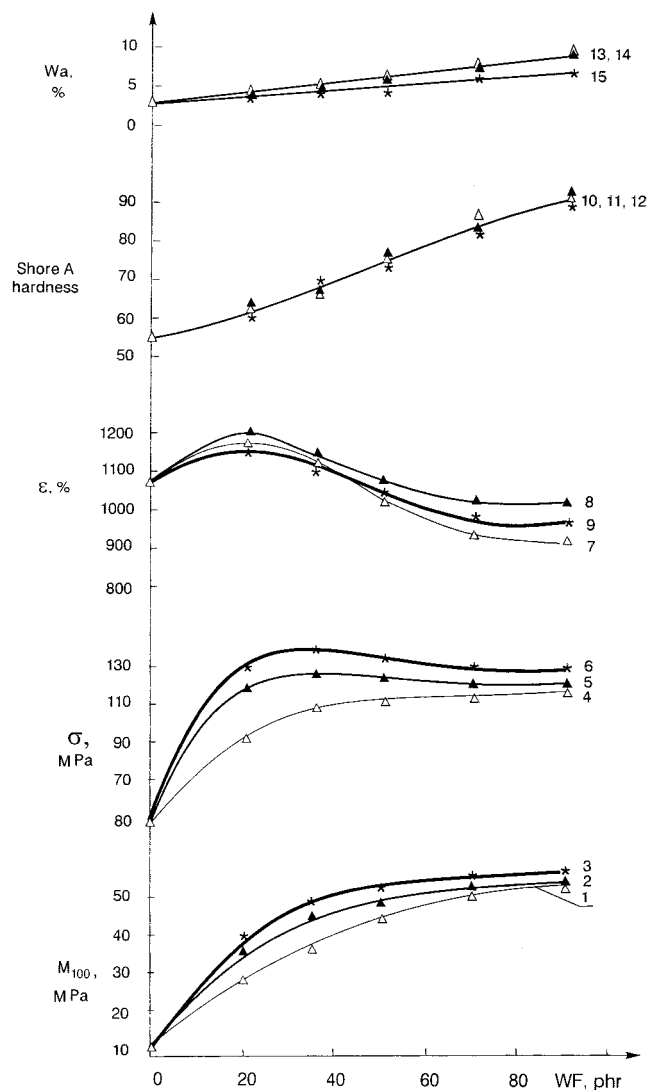


Figure 5 Mechanical parameters: modulus, M_{100} (curves 1–3), tensile strength, σ (curves 4–6), elongation at break, ε (curves 7–9), and Shore A hardness (curves 10–12) and water adsorption, W_a (curves 13 and 14) of wood flour-filled NBR compounds, containing 15 phr PFAR (with 5 phr hexamethylenetetramine/100 phr resin), added together with conifer wood flour (curves 1, 4, 7, 10, and 13) or just before it (curves 2, 5, 8, 11, and 14). Curves 3, 6, 9, 12, and 15 correspond to NBR compounds containing the same amount (15 phr) of PFAR added just before the filler but the non-modified wood flour was replaced by corona-activated wood flour.

TABLE III
Changes in the Mechanical Parameters of the Studied NBR Compounds Filled by Nonmodified Wood Flour (WF) or CTWF in the Presence of Different Amounts of PFAR

Mixture No.	PFAR (phr/100 phr WF)	WF (phr/100 phr NBR)	CTWF (phr/100 phr NBR)	Parameter			
				M_{100} (%)	σ (%)	ε (%)	Shore A (unit)
1	—	—	—	+7.0	-13.6	-20.0	+7
2	10	20	—	+5.2	-6.0	-18.9	+5
3	10	35	—	+4.9	-5.8	-16.1	+5
4	10	50	—	+3.9	-9.2	-15.6	+6
5	10	70	—	+6.0	-7.0	-15.0	+6
6	10	90	—	+5.1	-5.3	-14.1	+6
7	15	20	—	+4.8	-5.3	-11.3	+5
8	15	35	—	+5.0	-4.8	-12.3	+6
9	15	50	—	+4.2	-3.9	-12.6	+5
10	15	70	—	+5.6	-4.6	-12.7	+4
11	15	90	—	+3.9	-4.3	-11.9	+3
7'	15	20	—	+4.0	-4.2	-10.6	+3
8'	15	35	—	+4.6	-3.5	-12.8	+4
9'	15	50	—	-1.6	-3.9	-11.6	+5
10'	15	70	—	+5.2	-4.1	-11.3	+6
11'	15	90	—	+4.0	-3.6	-11.0	+3
7''	15	—	20	+3.6	-3.4	-10.2	+2
8''	15	—	35	-2.9	-3.6	-10.6	+3
9''	15	—	50	+5.0	-2.9	-11.0	+4
10''	15	—	70	+5.3	-3.0	-10.1	+6
11''	15	—	90	+4.0	-2.0	-9.6	+6
12	20	20	—	+2.3	-1.1	-6.2	+2
13	20	35	—	+3.0	-2.0	-8.4	+1
14	20	50	—	-1.0	-0.8	-7.0	+2
15	20	70	—	+2.2	-1.2	-6.5	+3
16	20	90	—	+2.1	-2.2	-5.2	+1

curves 10 and 11 in Fig. 5) and the water adsorption (compare curves 13 and 14 in Fig. 5) do not change significantly as was expected.

The replacement of the nonmodified wood flour by corona-treated wood flour in the filled NBR compounds containing 15 phr PFAR, added just before the filler, leads to an additional increase of the modulus M_{100} (compare curves 2 and 3 in Fig. 5), and the tensile strength, σ (compare curves 5 and 6 in Fig. 5), and to a slight decrease of the elongation at break, ε (compare curves 8 and 9 in Fig. 5). Both the surface etching that increases the surface roughness and hence the geometric area and the surface oxygen-containing groups accumulation increasing the surface polarity of the corona-treated wood flour particles¹¹ could explain the additional improvement of the mechanical parameters of the PFAR-containing NBR compounds, at which the nonmodified wood flour is replaced by a corona-activated one. The changes of Shore A hardness (compare curves 11 and 12 in Fig. 5) and the water adsorption, W_a (compare curves 14 and 15) are insignificant. Evidently, the corona treatment of the wood flour turns it into a semiactive filler in NBR compounds containing PFAR. The same was concluded earlier for the corona-treated wood flour-filled NBR compounds not containing PFAR¹¹. The general description and control of the plasma-chemical surface modification of different

materials is too complicated because of the very large variety of plasma-chemical processes leading to surface etching and surface chemical compound and polarity changes. This is the reason we are performing structural and chemical analyses to characterize the corona-modified wood flour. The results of our scanning electron microscopy observations, contact angles with polar and nonpolar liquids measurements, the surface tension and polarity calculation, electron spectroscopy for chemical analysis (ESCA) surface analyses of wood flour, corona treated under different operating conditions (including treatment voltage, duration, and medium) as well as its effect in rubber matrices with opposite polarity will be published in future papers.

It appears, that wood flour-filled NBR compounds with increased modulus, M_{100} (up to about 5–6 times), tensile strength, σ (up to about 2.5–3 times), and Shore A hardness (up to about 90) could be obtained using corona-activated wood flour in combination with PFAR (15 phr/100 phr wood flour). Such vulcanisates (see curve 15 in Fig. 5) demonstrate relatively low water adsorption (in the range of 3–8%), which is due to both the presence of the PFAR in the studied NBR compounds and the complete encapsulation of the wood flour particles in the rubber matrix.

The changes of the mechanical parameters after aging (70°/168 h) of the studied NBR compounds are presented in Table III. No clearly expressed regularity is observed, but it is evident that all compounds containing PFAR (mixtures 2-16; 7'-12' and 7'-12" in Table III) filled by nonmodified (mixtures 2-16; 7'-12' in Table III) or corona-treated (mixtures 7'-12" in Table III) wood flour have increased thermal-oxidative stability compared to the control mixture (mixture 1 in Table III) that does not contain nor PFAR or wood flour. Such a result is not surprising because 1) the PFAR usually increases^{5,6} the aging resistance of the rubber and 2) the wood flour does not influence significantly the aging resistance of the NBR vulcanisates¹.

CONCLUSION

It was established that the PFAR affects considerably the cure characteristics and the mechanical properties of the wood flour-filled NBR compounds due to a presumable action as an interface interactions modifier. It improves also their thermal-oxidative stability, acting as an antiaging agent.

The optimal PFAR amount with regard to the cure characteristics and mechanical parameters is about 15 phr/100 phr wood flour.

The addition of PFAR just before the wood flour is to be preferable because of both its better homogenization in the rubber matrix and its lower adsorption by the wood flour, leading to an improvement of the mechanical properties of the wood flour-filled NBR compounds.

The replacement of nonmodified by corona-treated wood flour leads to additional increase in the M_{max} , the ΔM , and the mechanical parameters without significant change of the optimum cure time, aging resistance, and water adsorption.

The inclusion of an optimal PFAR amount (15 phr/100 phr rubber) in the NBR compounds filled by corona-activated wood flour offers a possibility for obtaining vulcanisates with a sharply increased modulus, M_{100} (up to about 6 times), tensile strength, σ (up to about 3 times), and Shore A hardness (with up to 35 units), having simultaneously improved aging resistance and decreased water adsorption.

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