Wood Flour: A New Filler for the Rubber Processing Industry. I. Cure Characteristics and Mechanical Properties of Wood Flour-Filled NBR And NBR/PVC Compounds

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Received 28 January 2001; accepted 30 July 2003

ABSTRACT: In this study, conifer wood flour was evaluated as a filler to NBR or NBR/PVC compounds studying it influence on their cure characteristics and mechanical properties. It was shown that the filling by wood flour offers a possibility to obtain high modulus high elastic or less elastic or rigid wood like vulcanizates by varying of both the filling level and NBR/PVC mass ratio.It was established that in contrary to the mineral fillers usually causing significant delay of the vulcanization process, the wood flour shows a tendency to reduce the optimum cure time, τ_{90}. Modulus M_{100} and Shore hardness of the wood flour-filled vulcanizates of NBR or NBR/PVC compounds in which NBR is predominant, increase in a compliance with the increase of M_{max} and DM when the filling level increases. The dependence is other when NBR and PVC are in equal amounts or PVC predominates. As a most probable explanation of the effect of the wood flour on the cure characteristics is accepted, the influence of the wood flour polar groups as well as of the presenting as wood flour humidity water molecules, the specific mechanical properties of the wood flour-filled NBR or NBR/PVC compounds could be connected (to some extend) with a specific interface interaction between the wood flour particles and the polymer matrix. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2734–2739, 2003

INTRODUCTION

The well-known disadvantages of the most conventional rubber filler, carbon black, are the incentives of the tendency today to be replaced by silica or other fillers. The progress in the use of nonconventional fillers is mainly due to a successive regulation of the rubber matrix/filler particles interface interaction thorough a filler surface modification. The first tyres made by silica-filled rubber have already been reported.

Waste wood is an important biomass resource. The rising oil prices and the high energy requirements in the production of synthetic polymers urge the future use of the waste wood in material applications rather than for energy production. Many research groups have been studying new ways to utilize waste wood during the last few years. Waste wood and some other lignocellulosics, such as wheat straw or barks of different tree species, have been converted into thermosetting moulding materials.[1–7] New wood–polymer materials like, for example, the commercialized artificial wood on the base of wood flour-filled PVC,[8–11] have been obtained as a result of some theoretical and new technological solutions. Wood-based fillers yield composites with lower density and abrasiveness to the processing equipment as well as with an improved biodegradability compared to the inorganic one.[13] However, the properties of the filled plastics depend on the wood type, the filler particles shape and size, the level of filling, the processing conditions, the surface treatment of the filler particles modifying the polymer matrix/filler particles interface interaction, etc.[12–19]

Scant information about the effect of wood-based fillers in rubber compounds could be found only in the technical literature. The reinforcing effect of a carbon black/mica filler in NBR as well as in NBR/PVC compounds has been investigated by Nagay and Erman.[19] The effect of mica replacement by wood flour on the mechanical properties, swelling, and cure behavior of the corresponding composites has been discussed in the same article. Utilization of wood floor made by conventional grinding of amortized railway traverses, as a filler in thermosetting epoxy resin/rubber compounds for a high-quality traverses production has been described elsewhere.[20] But systematic investigations on the effect of wood flour in rubber as well as in rubber/plastic compounds are missing. Therefore, in this study, we aimed at evaluating the wood flour (nonmodified or modified) as an important filler in the making of high-value rubber or rubber/plastic composite materials, placing our emphasis mainly at the basic technological and exploitation characteristics of the filled compounds.

Some preliminary experiments, carried out by us to estimate the mixing ability of the wood flour with both

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Journal of Applied Polymer Science, Vol. 90, 2734–2739 (2003)

nonpolar and polar rubbers, showed its excellent ability to mix with all widely used rubbers: NR, IR, SBR, BR, NBR, and chloroprene rubber.

Our first announcement is concerning the effect of nonmodified conifer wood flour on the cure characteristics and mechanical properties of NBR as well as NBR/PVC compounds.

EXPERIMENTAL

Nitrile butadiene rubber (NBR 40, manufactured in Russia, with parameters according to Russian standard GOST 7738/79), Polyvinylchloride (PVC-S 64, manufactured by Devnya Chemical Combine, Bulgaria, with parameters according to Bulgarian standard 8806-71) and conifer wood flour (manufactured by Firm "Maritsa," Kostenets, Bulgaria, with parameters according to Bulgarian standard 3718-74, with particle sizes of 60–100 mm and a humidity of 6%) were used in this study. The model NBR compounds contain traditional ingredients (phr): NBR-40, 100; wood flour—varied; stearic acid, 2; zinc oxide, 3; sulphur, 2; sulphenamide accelerator (Vulkacit CZ, Bayer), 2. The model NBR/PVC compounds contain the same ingredients in the same amounts but calculated to 100 phr NBR excluding the wood flour. The variables, wood flour amount and NBR/PVC mass ratio, are shown in Tables I and II. All the materials used were of standard rubber industry grade and not purified for this study.

NBR/PVC mass ratio was varied in a way giving one of each type of the compounds: (1) with a predominant amount of NBR, NBR/PVC = 80/20 phr, (2) with equal amounts of NBR and PVC NBR/PVC = 50/50 phr, and (3) with a predominant amount of PVC, NBR/PVC = 40/60.

The model mixtures were prepared on laboratory roll mill with a friction ratio of 1 : 1.4 in a conventional way. The wood flour was added at the first preparation stage and PVC—before all other ingredients.

The microscope photographs are taken down from nonvulcanized samples in polarized light using a MBI-6 microscope. The electron photomicrographs are taken down from carbon replica of the fragile fracture surface of the corresponding vulvanisate using a Philips EM 400 apparatus.

The vulcanization characteristics were determined according to Bulgarian standard 15754-83 with a Monsanto Rheometer MDR 2000 at 160°C. The vulcanization was carried out at this same temperature and the optimum cure time.

TABLE I
NBR Compounds with A different Wood Flour (WF) Levels

Mix no.	1	2	3	4	5
WF, phr	0	35	50	70	90

TABLE II
NBR/PVC Compounds with a Different NBR/PVC Mass Ratio and Wood Flour (WF) Levels

NBR/PVC, mass ratio	WF, phr				
80/20	0	35	50	70	90
50/50	0	35	50	70	90
40/60	0	35	50	70	90

The mechanical parameters were determined according to ISO/R37 and the heat aging—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 to the following formula:

$$W_a = (P_1 - P_0) \cdot 100 / P_0, \%$$

where W_a is the the water adsorption, P_0 is the the weight of the sample before testing, and P_1 is the weight of the sample after keeping it in water.

The IR spectrum of the conifer wood flour was taken down from a KBr tablet with a Perkin-Elmer FTIR Spectrometer 1600.

RESULTS AND DISCUSSION

The visual observation of the mixing process showed an excellent wood flour intake and homogenization of the NBR and NBR/PVC compounds as well as a possibility for a relatively high degree of filling—up to 90–100 phr even in the absence of any process aid for a large volume of filler incorporation. The wood flour disperses very uniformly in the polymer matrix (NBR or NBR/PVC mixture), independent on the filling level, as it was demonstrated by our microscopy observation (Fig. 1). The detailed electron microscope photographs (Fig. 2) showed that the wood flour particles incorporated in the polymer matrix are not associated (maybe due to their specific branched shape), and they are very well wetted by the matrix polymer. The last one confirms by the relatively low water adsorption of all wood flour filled compounds (it does not surpass 9.3 wt % in all cases) and its similarity to that of the corresponding control nonfilled compounds (up to about 8 wt %) (Tables VIII and IX). The processability of the wood flour filled compounds is comparable to that of the carbon black-filled one. For example, the processability coefficient, λ, and the homogenation time, t (estimated from Brabender plastograms) of the model NBR compounds filled with 35 phr conifer wood flour or 35 phr carbon black, FEF are respectively: λ—0.27 or 0.29, and t (min : s)—2 : 50 or

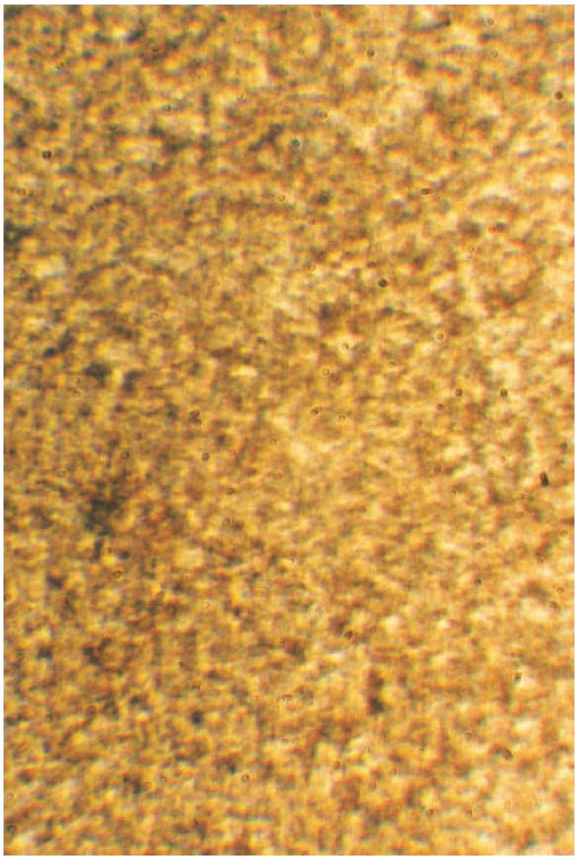

Figure 1 General appearance of the wood flour dispersion in the polymer matrix (×90). NBR filled with 50 phr conifer wood flour. All other samples are similar, and therefore, their photographs are not represented here.

Figure 2 Electron photomicrograph of wood flour particles in the polymer matrix (NBR with 50 phr conifer wood flour).

3 : 10. All nonvulcanized mixtures and the corresponding vulcanizates are wood like. The vulcanizates are high elastic or less elastic or even rigid, depending on both the filling level and the mass ratio NBR/PVC.

Cure characteristics

The cure characteristics of NBR compounds containing different wood flour amounts are represented in Table III. It is evident that, in opposition to the mineral fillers leading to significant increase of the optimum cure time, t_{90}, the wood flour decreases it. Simultaneously, M_{min}, M_{max}, and $\Delta M = M_{max} - M_{min}$ show a tendency to increase, better expressed at higher filling levels (Table III, mixes 2–5 to mix 1). The differences observed in the optimum cure time of the nonfilled (Table III, mix 1) and wood flour-filled compounds (Table III, mix 2–5) could be accepted as an indication for the existence of a significant interface interaction between the rubber matrix and the wood flour particles.[21,22] As it is well known, the cellulose molecules contain a lot of methylol and hydroxyl groups, and the wood wool contains phenolyc, ester, and carboxyl groups.[23,24] An additional confirmation in this respect is an IR spectrum of the studied conifer wood flour shown by us (Fig. 3) containing the following absorption peaks: 3600–3100 cm^{-1} (νOH associated with hydrogen bonds); 3100–3000 cm^{-1} (νCH in Ar); 2960–2850 cm^{-1} (νCH in CH_2 and CH_3); 1730 cm^{-1} (νCO); 1600 cm^{-1}, 1500 cm^{-1}, and 1450 cm^{-1} (νC═C in Ar core); 1400 cm^{-1} (νCH in CH_2 and CH_3); 1370–1360 cm^{-1} (νCH in CH_3); 1150–850 cm^{-1} (ηC—O—C in the ring and νC—O in C—OH). The peaks ascription was made according to ref. 25. It is known[26–29] that the polar substances (including the water) influence significantly the cure process. Therefore, the influence of the wood flour on the cure characteristics of the filled NBR compounds could be ascribed to the above-described filler's polar oxygen containing groups as well

TABLE III
Cure Characteristics of NBR Compounds with Different Wood Flour (WF) Levels

Mix no.	WF, phr	M_{min}, dNm	M_{max}, dNm	ΔM, dNm	t_{s1}, min:sec	t_{90}, min:sec	V_c, % · min^{-1}
1	0	7.0	40.0	23.0	3:10	7:10	25.0
2	35	10.0	57.0	47.0	2:20	5:20	33.3
3	50	11.0	59.0	48.0	2:20	6:00	27.8
4	70	11.5	65.0	53.5	2:10	6:30	24.4
5	90	13.5	81.5	68.0	2:20	5:00	37.0

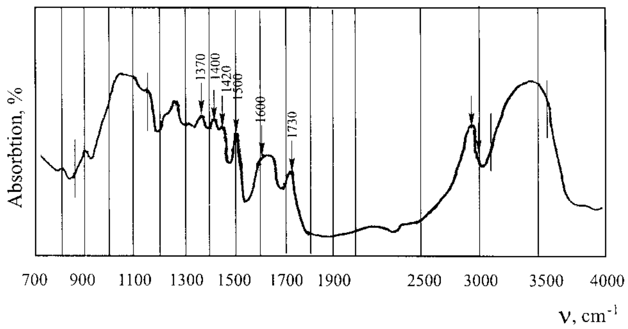

Figure 3 IR spectrum of a conifer wood flour.

as of the water molecules presenting in the wood flour as its humidity.

It is evident from Table IV, that as in the case of nonfilled and wood flour-filled NBR compounds, the optimum cure time, t_{90} of all wood flour-filled NBR/PVC compounds is shorter compared to that of the corresponding nonfilled compounds with the same NBR/PVC mass ratio (compare mix 7–10 and 6; 12–15 and 11; 17–20 and 16, Table IV.). A comparison of the NBR compounds optimum cure time, t_{90} and cure rate, Vc (Table III, mixes 1–5) to these parameters of the NBR/PVC compounds shows that the vulcanization process is additionally accelerated in presence of PVC. M_{min} is higher for all NBR/PVC-based compounds compared to NBR-based one (Table III, mixes 1–5 and Table IV, mixes 6–20), and it increases with an increase in the wood flour level in any cases (Table IV, mixes 6–10; 11–15, and 16–20). M_{max} and $\Delta M = M_{max} = M_{min}$ increase slightly with increase the wood flour level when NBR is predominant (Table IV, mixes 6–10) or equal to PVC (Table IV, mixes 11–15), and they decrease when PVC get predominant (Table IV, mixes 16–20) in the NBR/PVC polymer matrix. The differences observed in the cure characteristics of the studied compounds indicate the influence of the nature of the polymer matrix (NBR or NBR/PVC in different mass ratios) and the wood flour filling level.

TABLE V
Mechanical Parametrs of NBR Vulcanizates with Different Wood Flour (WF) Levels

Mix no.	*WF*, phr	M_{100}, MPa	σ, MPa	ε, %	Hardness shore A
1	0	10.6	36.2	1140	55
2	35	14.0	42.1	970	70
3	50	21.2	33.6	814	72
4	70	27.1	32.0	512	75
5	90	39.0	30.3	500	76

Mechanical properties, aging

The mechanical parameters of the vulcanizates based on NBR compounds of different wood flour levels are given in Table V. It is evident that the modulus, M_{100} and Shore hardness A increases, whereas the elongation at break, ϵ decreases significantly with increasing the wood flour level. Simultaneously, the tensile strength, σ decreases slightly. The increase of the hardness and modulus is evidently due to the reduction of the volume fraction of the elastomer. The simultaneous decrease of the tensile strength and elongation at break indicates that the nonmodified conifer wood flour could be classified to the nonreinforcing fillers. The dependence of the same parameters on the wood floor level is similar for the vulcanizates based on NBR/PVC compounds in which NBR is predominant (mass ratio 80/20) (Table VI, mixes 6–10). Modulus, M_{100} stays almost constant, tensile strength, σ, and Shore hardness increases slightly and elongation at break, ϵ, decreases when the NBR/PVC mass ratio is 50/50 (Table VI, mixes 10–15). Modulus, M_{100} and

TABLE IV
Cure Characteristics of NBR/PVC Compounds of Different NBR/PVC Ratios and Wood Flour (WF) Levels

Mix no.	NBR/PVC, mass ratio	WF, phr	M_{min}, dNm	M_{max}, dNm	ΔM, dNm	t_{s1}, min:sec	t_{90}, min:sec	V_c, % · min^{-1}
6		0	11.5	59.0	47.5	3:00	5:00	50.0
7		35	14.5	75.0	60.5	3:00	4:20	76.9
8	80/20	50	15.5	75.0	59.5	2:20	4:00	58.8
9		70	17.5	81.2	63.5	2:10	3:25	77.0
10		90	18.0	83.0	65.0	2:00	3:10	86.9
11		0	12.8	62.8	50.0	3:00	4:20	83.3
12		35	17.0	77.1	60.1	2:20	3:25	86.8
13	50/50	50	19.1	79.0	59.9	2:00	3:10	86.9
14		70	22.0	85.3	63.3	2:00	3:20	76.9
15		90	23.0	85.0	62.0	2:10	3:20	86.9
16		0	13.1	64.2	51.1	2:50	4:10	83.3
17		35	18.5	73.5	55.0	2:25	3;25	100.0
18	40/60	50	22.5	61.0	38.5	2:20	3:20	100.0
19		70	22.0	58.0	36.0	2:20	3:20	100.0
20		90	24.0	60.1	36.1	2:10	3:10	100.0

TABLE VI
Mechanical Parameters of NBR/PVC Vulcanizates with Different NBR/PVC Mass Ratio and Wood Flour (WF) Levels

Mix, no.	NBR/PVC, mass ratio	WF, phr	M_{100}, MPa	σ, MPa	ε, %	Hardness shore, A
6		0	29.6	61.2	910	63
7		35	37.0	77.8	520	79
8	80/20	50	38.1	64.3	470	80
9		70	38.3	50.2	430	82
10		90	49.0	49.9	368	84
11		0	39.5	80.1	620	85
12		35	39.0	94.3	306	89
13	50/50	50	38.5	94.8	300	90
14		70	37.5	107.0	160	92
15		90	37.0	118.2	150	92
16		0	64.2	71.8	305	90
17		35	120.0	121.3	150	93
18	40/60	50	126.6	135.0	132	93
19		70	—	—	—	95
20		90	—	—	—	95

tensile strength, σ increases sharply and elongation at break decreases when PVC is predominant in the polymer matrix–mass ratio 40/60 (Table IV, mixes 16–20). The differences observed in the mechanical properties of the filled NBR/PVC vulcanizates in which the ratio between NBR and PVC is different evidently are connected with the nature of the polymer matrix.

The next Table VII shows that the changes in the mechanical properties of the vulcanizates based on wood flour-filled NBR or NBR/PVC compounds are

TABLE VII
Changes in the Mechanical Parameter of NBR and NBR/PVC Wood Flour (WF) Filled Vulcanizates after ageing for 168 h at 70°C

Mix no.	NBR/PVC, mass ratio	WF, phr	M_{100}, %	σ, %	ε, %	Hardeness shore A
1		0	+6.1	−11.2	−15.9	+3
2		35	+7.7	−0.8	−11.2	+3
3	100/0	50	−3.6	−11.0	−16.2	+6
4		70	+6.5	−9.9	−10.9	+2
5		90	+9.1	−10.3	−17.8	+4
6		0	+9.2	−9.8	−20.1	+6
7		35	+4.9	−10.0	−12.5	+4
8	80/20	50	+7.3	−12.3	−14.5	+6
9		70	+(.3	−8.1	−16.1	+7
10		90	+6.4	−8.6	−11.9	+2
11		0	+8.7	−13.8	−19.8	+6
12		35	+9.6	−11.2	−11.3	+4
13	50/50	50	+1.9	−10.3	−10.9	+2
14		70	+10.3	−8.6	−11.1	+8
15		90	+9.3	−15.1	−10.9	+3
16		0	+1.2	−9.4	−6.2	+3
17		35	+3.3	−10.0	−4.1	+2
18	40/60	50	+12.1	−2.9	−6.9	+6
19		70	—	—	—	+2
20		90	—	—	—	+1

TABLE VIII
Water Adsorbtion and Density of NBR Wood Flour (WF)-Filled Vulcanizates

Mix no.	WF, phr	Water adsorption, %	Density, g/cm^3
1	0	8.0	1.20
2	35	8.8	1.15
3	50	9.3	1.15
4	70	8.9	1.10
5	90	9.0	1.10

almost the same as compared to those of the corresponding nonfilled compounds after thermal aging for 168 h at 70°C. These results give reason to conclude that the filling of NBR or NBR/PVC compounds by wood flour does not get worse with their aging resistance.

Water adsorption

Water adsorption of both the wood flour-filled NBR and NBR/PVC compounds is generally low (below 9.3 wt.%) indicating that the wood flour particles are well encapsulated in the polymer matrix. But the water adsorption of all wood flour-filled compounds is a little bit higher compared to those of the corresponding nonfilled compounds, and it increases slightly with increase of the wood flour filling level (Tables VIII and IX). This effect could be connected with the presence of a small amount surface semiencapsulated wood flour particles and their hydrophilic nature as well as with the a little bit lower density of the wood flour-filled vulcanizates. Evidently, wood flour needs in appropriate surface hydrophobization when one wants to obtain vulcanizates with lower water adsorption.

TABLE IX
Water Adsorbtion and Density of NBR/PVC Wood Flour (WF)-Filled Vulcanizates

Mix no.	NBR/PVC mass ratio	WF, phr	Water adsorption, %	Density, g/cm^3
6		0	6.4	1.30
7		35	7.2	1.20
8	80/20	50	7.9	1.15
9		70	8.1	1.15
10		90	8.6	1.10
11		0	5.6	1.40
12		35	6.0	1.35
13	50/50	50	6.3	1.30
14		70	6.0	1.30
15		90	7.2	1.25
16		0	5.3	1.40
17		35	5.7	1.30
18		50	6.0	1.25
19	40/60	70	6.1	1.20
20		90	6.1	1.10

CONCLUSIONS

The filling of NBR or NBR/PVC compounds by wood flour offers a possibility to obtain high modulus high elastic or less elastic or rigid wood-like vulcanizates by varying both the filling level and NBR/PVC mass ratio.

The cure characteristics of the wood flour-filled NBR or NBR/PVC compounds indicate that, in contradiction to the mineral fillers, usually causing significant delay of the vulcanization process, the wood flour demonstrates a tendency to accelerate it. The effect of the wood flour on the cure characteristics is explained with the influence of the wood flour polar groups and the presence of water molecules as a wood flour humidity.

The mechanical parameters, modulus M_{100} and Shore hardness and the water adsorption of both NBR or NBR/PVC compounds increase, whereas the tensile strength and elongation at break decrease with the increase of the filling level. The simultaneous decrease of the tensile strength and elongation at break gave us reason to ascribe the nonmodified conifer wood flour to the inert rubber fillers.

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