Wood Flour: A New Filler for the Rubber Processing Industry. II. Cure Characteristics and Mechanical Properties of NBR Compounds Filled with Corona-Treated Wood Flour

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ABSTRACT: Corona-treated wood flour was evaluated as a filler for NBR (nitrile butadiene rubber) compounds by studying its influence on their cure characteristics and mechanical properties. The different operating conditions of the corona treatment, such as voltage and duration, which led to different degrees of surface etching, were observed by means of electron microscopy. Accumulation of different oxygen-containing groups on the wood flour particles' surface was confirmed by means of ESCA. Wood flour–filled materials were thus obtained with varying final properties. The cure characteristics, mechanical parameters, and water adsorption of the composites were estimated to determine an optimum level of the wood flour surface modification. The corona treatment of the wood flour renders it into a semiactive filler. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 883–889, 2004

Key words: corona-treated wood flour; filled NBR compounds; cure characteristics; mechanical properties; fillers

INTRODUCTION

In a previous investigation[1] we studied the effect of nonmodified conifer wood flour in nitrile butadiene rubber (NBR) and NBR/poly(vinyl chloride) (PVC) compounds. We found that filling compounds with wood flour offers the possibility of obtaining high modulus, highly elastic or less elastic, or rigid wood-like vulcanizates by varying both the filling level and the NBR/PVC mass ratio. Generally nonmodified wood flour acts as a nonreinforcing filler. During the past few decades, there has been increasing interest in surface engineering of filler particles aimed at improving the interface interaction of filler particles/polymer matrix and thus the filled polymers' properties.

There are a number of reports in the literature about wood chemical modification oriented mainly toward increasing the hydrophobicity of wood. For example, Domininghaus[2] reported on the impregnation with vinyl monomers followed by drying and a radical polymerization. Other authors described an impregnation by phenolformaldehyde resin,[3,4] furfural, [5] or some wood extracts,[6] for example.

Lately some studies have reported about the chemical modification of cellulose fibers that improves their interaction with rubber matrices. Flink and Stenberg[7] grafted allyl acrylate or allylmethacrylate onto short cellulose fibers that resulted in better wetting and increased adhesion to a natural rubber (NR) matrix. Ahlblad et al.[8] grafted butadiene or divinylbenzene by plasma treatment. The formation of a layer on the fibers' surface, which is a conceivable way of improving the mechanical properties of NR composites, has been achieved. However, a more homogeneous activated fiber surface has been obtained by electron irradiation instead of the more variable plasma technique.[9] Nowadays, it seems that the natural fiber–reinforced polymers have made a comeback.[10]

Scanty information about wood flour modification directed to its application as a soft filler in polymer composites or rubber compounds may be found in the technical literature. Marcovich et al.[11] esterificated wood flour and used it as a thermosetting filler for unsaturated polyester–styrene resins. Alma and Shirashi[12] phenolated (in the presence of sulfuric acid as a catalyst) birch wood flour and tested the obtained phenolated wood resin as a thermosetting material. Corona treatment is a commercially implemented method for oxidative treatment of polymers.[13,14] Surface etching and accumulation of oxygen-containing groups develop simultaneously during treatment in the range of oxygen-containing cold plasma (Fig. 1).

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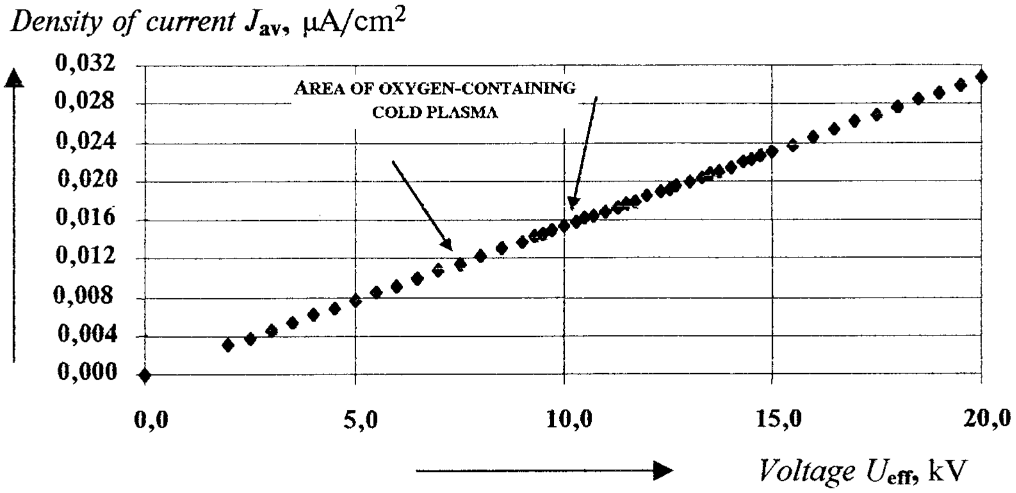

Figure 1 Range of the oxygen-containing cold plasma obtained in corona discharge in air.

Such treatment changes the whole complex of surface physicochemical properties of the treated material including its surface polarity. Porous polymeric materials, such as wood flour, are very suitable for corona discharge treatment because of their plasma permeability. We demonstrate here how some wood flour surface properties are affected by treatment in cold oxygen-containing plasma obtained in a corona discharge and the change in the cure characteristics and mechanical properties of the respective wood flour–filled NBR compounds.

EXPERIMENTAL

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

The model NBR compounds contain traditional ingredients (phr): NBR 40, 100; wood flour (nontreated or corona treated), 50; stearic acid, 2; zinc oxide, 3; sulfur, 2; and sulfenamide accelerator (Vulkacit CZ, Byer), 2. All the materials used were of standard rubber industry grade and used as received for this study.

The modified wood flour was prepared by corona treatment in air under the following conditions: thickness of the wood flour layer, 4 mm; the variables, voltage, and duration of the corona treatment are shown in Table I.

The model mixtures were prepared on a laboratory roll mill with a friction ratio of 1 : 1.4 by conventional process. The wood flour was added at the first preparation stage.

Vulcanization characteristics were determined according to Bulgarian standard 15754-83 with a Monsanto Rheometer MDR 2000 (Monsanto, St. Louis, MO) at a temperature of 170°C. The vulcanization was carried out at this same temperature and optimum cure time.

Mechanical parameters were determined according to ISO/R37 and the heat ageing, according to ISO/188.

Water adsorption (%Wa) was measured using 50 × 50 × 2-mm samples kept in distilled water for 24 h. The corresponding calculations were performed according to the following formula:

$$\%Wa = \frac{P_1 - P_0}{P_0} \times 100$$

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 being kept in water.

The electron microscopy photographs were taken by direct observation of wood flour particles using a Philips EM 400 apparatus (Philips, The Netherlands).

TABLE I
Values of the Operation Parameters of the Corona Discharge

Mix no.	Voltage (kV)	Duration (min)
1	—	—
2	6	3
3	6	5
4	6	10
5	6	15
6	8	3
7	8	5
8	8	10
9	8	15
10	10	3
11	10	5
12	10	10
13	10	15

TABLE II
Cure Characteristics of NBR Compounds Filled with 50 phr Nontreated or Corona-Treated Conifer Wood Flour, Under Different Voltages and Durations

Mix no.	Voltage (kV)	Duration (min)	$M_{\min}$ (Nm)	$M_{\max}$ (Nm)	ΔM (Nm)	t_{s2} (min:s)	t_{90} (min:s)	V_c (% min^{-1})
1	—	—	6	46	40	1:50	5:50	25.0
2	6	3	6	48	42	2:00	6:10	24.4
3	6	5	6	47	41	1:50	5:20	28.6
4	6	10	6	47	41	2:10	5:10	33.3
5	6	15	6	46	40	2:10	5:20	32.3
6	8	3	6	47	41	2:10	5:10	33.3
7	8	5	6	48	42	2:10	5:10	33.3
8	8	10	6	48	42	2:00	5:00	33.3
9	8	15	6	51	45	1:50	4:50	33.3
10	10	3	6	50	44	1:50	4:50	33.3
11	10	5	6	51	45	1:50	4:40	35.7
12	10	10	6	51	45	1:50	4:10	43.5
13	10	15	6	48	42	2:00	5:20	30.3

The real density ρ_r was measured picnometrically and the pore volume V_p was measured with mercury porosimetry.[15] The porosity α and the apparent density ρ_a were calculated, respectively, as:

$$\alpha = \frac{V_p}{V_p + V_w}$$

where $V_w = 1/\rho_r$ is the specific volume of the wood.

$$\rho_a = \rho_r(1 - \alpha)$$

Changes of parameters $\Delta\rho_r$, ΔV_w, $\Delta\rho_a$, $\Delta\alpha$, or ΔV_p were calculated in a comparison with the corresponding parameters of the nontreated wood flour.

ESCA was performed on conifer wood plates (15 × 10 × 3 mm) using a Leibold Heraeus instrument (Al–K_α, excitation energy: 1486.6 eV). Complete spectral scans and detailed recordings of the main peaks were made at 6×10^{-9} Torr. The binding energy scale (E_B) was fixed by assigning $E_B = 285$ eV to the –CH_2– carbon C(1s) peak. Using this reference peak (referred to as C1 in the figure) and according to previous studies[16] the carbon chemical shifts for different oxygen-containing groups are as follows: C2: $\equiv C{-}O{-}$ from hydroxyl or ether, $\Delta E_B = 1.5$ eV; C3: $=C{=}O$ from carbonyl, $\Delta E_B = 3.0$ eV; C4: –COO– from carboxyl, $\Delta E_B = 4.2$ eV.

RESULTS AND DISCUSSION

Cure characteristics

The cure characteristics of NBR compounds containing 50 phr nontreated (mixture 1) or corona-treated wood flour under different operating conditions (mixtures 2–13) are shown it Table II. It is evident that the corona treatment of the wood flour does not significantly affect the cure characteristics of the filled NBR compounds: the minimum torque ($M_{\min}$) value of all mixtures (control mixture 1 filled with 50 phr nontreated wood flour and mixtures 2–13 filled with the same amount of corona-treated wood flour) is about 6 nm; maximum torque ($M_{\max}$) changes in the range of 46–51 μm and ΔM in the range of 40–45 μm; the scorch time t_{s2} was 1.50–2.10 min; and the optimum cure time t_{90} was 4.40–6.10 min for all mixtures. A slight tendency of enhanced cure characteristics, that is, an increase of the $M_{\max}$, ΔM, and cure rate V_c, and reduction of the optimum cure time t_{90}, was observed with an increase of the voltage to 10 kV as well as of the treatment duration to about 10 min.

Mechanical properties, ageing

The mechanical parameters of the wood flour–filled vulcanizates of NBR compounds are shown in Figure 2. It is evident that the corona treatment of the wood flour at 6 kV for 3 to 15 min does not substantially change the mechanical parameters of the filled NBR compounds: the modulus M_{300} (Fig. 2, curve 1), the tensile strength σ (Fig. 2, curve 4), and the Shore hardness of the mixtures filled with modified wood flour are almost equal to those of the control mixture (the first point of the corresponding curves) filled with the same amount (50 phr/100 phr NBR) of nontreated wood flour. The elongation at break shows only a slight decrease when the treatment duration is about 10–15 min. The corona treatment of the wood flour at 8 or, better, at 10 kV significantly improves the efficacy of the wood flour: the modulus M_{300} (Fig. 2, curves 2 and 3) and the tensile strength σ (Fig. 2, curves 5 and 6) of the corona-treated wood flour–filled mixtures increase compared with the corresponding parameters of the control mixture. The modulus M_{300} and the

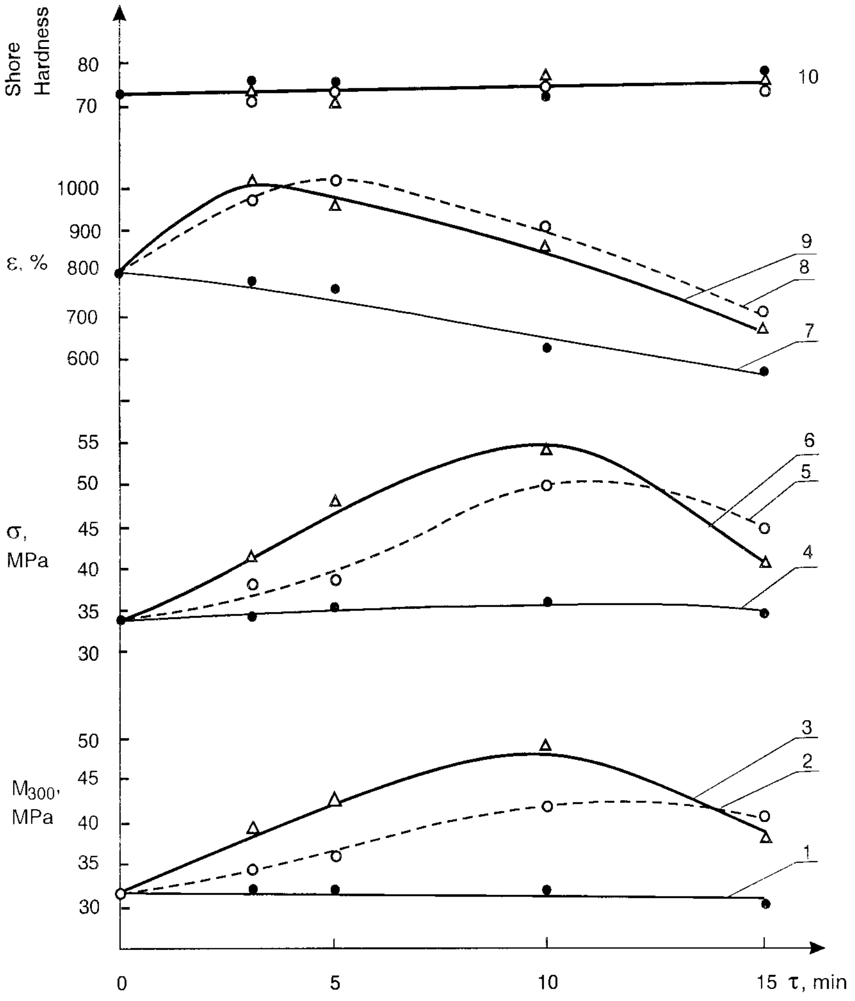

Figure 2 Mechanical properties: modulus M_{300} (curves 1, 2, and 3), tensile strength σ (curves 4, 5, and 6), elongation at break ϵ (curves 7, 8, and 9), and Shore hardness (curve 10) of NBR vulcanizates filled by 50 phr/100 phr rubber nontreated or plasma treated at 6 (curves 1, 4, 7, and 10), 8 (curves 2, 5, 8, and 10), or 10 kV (curves 3, 6, 9, and 10) wood flour.

tensile strength increased to about 45 or 60%, respectively, when corona-treated wood flour (at 10 kV for 10 min) was used instead of the same amount of nontreated wood flour. The elongation at break ϵ also demonstrates an increase when the duration of the corona treatment was about 10 min (Fig. 2, curves 8 and 9). The Shore hardness (Fig. 2, curve 10) is almost equal for all mixtures filled with nontreated or corona-treated wood flour at different operating conditions. This is in compliance with the almost equal degree of crosslinking (evaluated as ΔM from Monsanto rheograms) of all mixtures studied. Evidently, the optimal duration of the wood flour corona treatment is about 10 min for both voltages, 8 or 10 kV; the maximum of the M_{300} (Fig. 2, curves 2 and 3) and of the tensile strength σ (Fig. 2, curves 5 and 6) are at 10 min. The corona treatment at 10 kV is to be preferred because at this voltage the mechanical parameters of the filled NBR mixtures are maximal. When the NBR mixture contained 50 phr corona-treated wood flour at 10 kV for 10 min, its modulus M_{300} increased about 51% and the tensile strength about 60%, compared to the corresponding parameters of the control mixture filled with the same amount (50 phr) of nontreated wood flour. The Shore hardness is equal in both cases and the elongation at break ε is slightly increased when corona treatment was used at the same conditions. Table III shows that the changes in the mechanical parameters of NBR compounds filled with corona-treated wood flour (mixtures 2–13) are almost the same compared to the corresponding parameters of the control mixture (1) after ageing in air at 70°C for 168 h. This indicates that the corona treatment of the wood flour does not degrade the ageing resistance of the filled NBR vulcanizates.

Water adsorption

Water adsorption of NBR vulcanizates filled with 50 phr nontreated or corona-treated wood flour is repre-

TABLE III
Changes in the Mechanical Parameters of NBR Vulcanizates Filled with 50 phr Wood Flour, Nonmodified or Corona-Treated, Under Different Operating Conditions

Mix no.	Voltage (kV)	Treatment duration (min)	$\Delta\sigma$ (%)	$\Delta\varepsilon$ (%)	Shore hardness (units)
1	—	—	−11.0	−16.8	+4
2	6	3	−10.2	−20.4	+6
3	6	5	−9.9	−19.7	+3
4	6	10	−10.3	−12.9	+5
5	6	15	−11.8	−17.9	+7
6	8	3	−12.0	−20.1	+2
7	8	5	−10.9	−16.2	+6
8	8	10	−10.0	−17.9	+4
9	8	15	−9.3	−16.1	+5
10	10	3	−9.6	−17.9	+3
11	10	5	−10.1	−16.5	+5
12	10	10	−11.0	−12.0	+6
13	10	15	−12.2	−18.0	+4

sented in Table IV. It is evident that the water adsorption of all NBR vulcanizates is generally low (<11.6 wt %), indicating that the wood flour particles are well encapsulated within the rubber matrix. However, the water adsorption data demonstrate a tendency to slightly increase in the compounds containing corona-treated wood four compared to the control compound containing the same amount (50 phr) of nontreated wood flour (compare mixes 2–13 and mix 1 in Table IV). This could be attributable to some hydrophilicity of the corona-treated wood flour as a result of the accumulation of surface oxygen–containing groups. The wood flour must achieve appropriate surface hydrophobicity to obtain vulcanizates with lower water adsorption.

Electron microscopy observations

All changes observed in the mechanical parameters of the wood flour–filled NBR compounds could be the result of both the wood flour surface etching and the accumulation of surface oxygen–containing groups leading to changes in the interaction at the rubber matrix/filler particles interface.

Our comparative electron microscopy observation of nontreated and corona-treated wood flour particles demonstrated quite clearly the etching effect of the corona discharge. It is evident from Figure 3 that the treatment of the conifer wood flour in oxygen plasma obtained by corona discharge at the chosen operating conditions creates a surface roughness on the wood flour particles [compare Fig. 3(b) and (c) with Fig. 3(a)], expressed to a greater degree when the treatment time is extended by 10–15 min [compare Fig. 3(c) and (d) with Fig. 3(b)]. Such roughness results in an increased contact at the wood flour/rubber matrix surface area and usually improves the mechanical bonding attributed to the diffusion of the rubber within the volume of wood particles. The results of our electron microscopy observation substantially comply with the results of experimental estimation of the porosity of the nontreated and corona-treated wood flour.

Porosity of the wood flour

The data represented in Table V show that the corona treatment leads to a significant increase of the porosity of the wood flour: the porosity α (column 8) and the pore volume V_p (column 10) increase by about 67–101% (column 9) or 38–65% (column 11), respectively, whereas the volume of the wood substance V_w (column 4) decreases by about 17.9–19.7% (column 5). Increases in the real density ρ_r (column 2) and the apparent density ρ_a (column 6) indicate that the less-dense regions of the wood substance are removed during the etching, as expected. Evidently, the etching effect, confirmed both by our electromicroscopy ob-

TABLE IV
Water Adsorption of NBR Vulcanizates Filled with 50 phr Wood Flour, Nonmodified or Corona-Treated, Under Different Operating Conditions

	Mix number												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Density, g/cm^3	1.15	1.15	1.15	1.16	1.16	1.15	1.16	1.18	1.17	1.16	1.17	1.26	1.19
Water adsorption, %	9.4	9.3	9.5	10.0	9.7	9.2	10.3	9.6	10.3	9.6	9.4	11.6	11.1

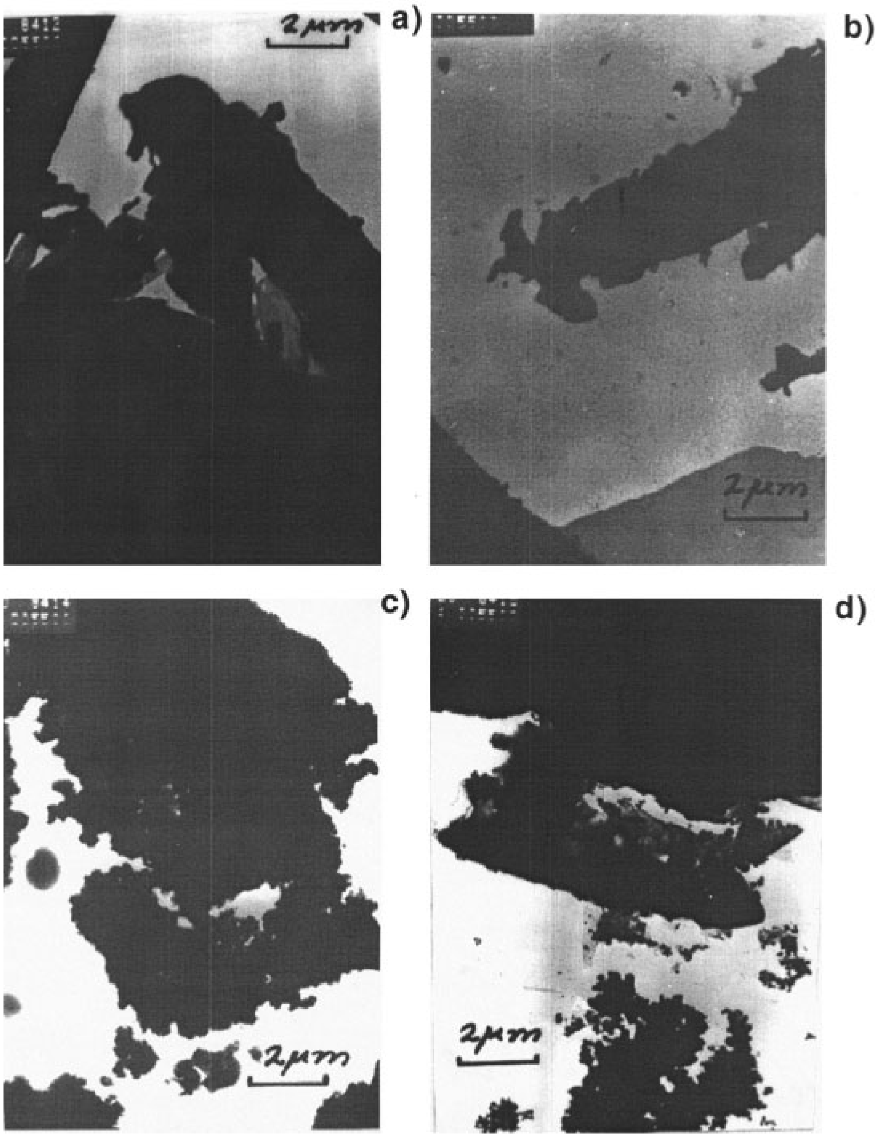

Figure 3 Electron microscopy photographs of (a) nontreated or plasma-treated wood flour particles at 10 kV for (b) 3 min, (c) 10 min, or (d) 15 min.

servation and by the wood flour porosity data, is one of the factors leading to the increased efficiency of the corona-treated wood flour with respect to the mechanical parameters of the filled NBR vulcanizates. Another reason for the observed changes in the mechanical parameters and the water adsorption of the NBR compounds, filled by corona-treated wood flour, could be the polarization of the surface of wood flour

TABLE V
Some Properties of the Nontreated and Corona-Treated Wood Flour at 10 kV

Treatment duration (min)	Real density, ρ_r (g/cm^3)	Change of real density, $\Delta\rho_r$ (%)	Volume of wood, V_w (cm^3/g)	Change of wood volume, ΔV_w (%)	Apparent density, ρ_a (g/cm^3)	Change of apparent density, $\Delta\rho_a$ (%)	Porosity, α (%)	Change of porosity, $\Delta\alpha$ (%)	Pore volume, V_p (%)	Change of pore volumeΔV_p (%)
Nontreated	1.2039	—	0.84160	—	1.1801	—	1.98	—	0.0170	—
3	1.4568	+21	.6857	−18.5	1.4078	+19.4	3.30	+67.0	0.0234	+38.0
5	1.4426	+19.8	0.6908	−17.9	1.3952	+18.2	3.29	+66.2	0.0235	+38.2
10	1.4961	+24.3	0.6755	−19.7	1.4366	+21.7	3.98	+101.0	0.0280	+64.7

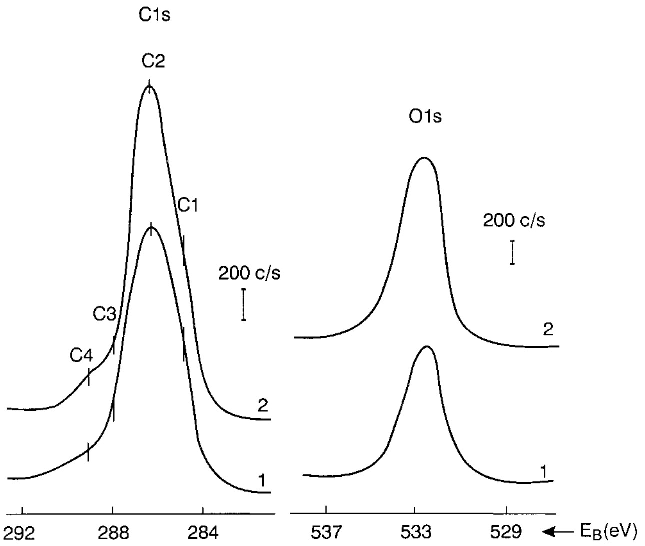

Figure 4 Detailed C(1s) and O(1s) ESCA peaks of nontreated (curves 1) or corona-treated (curves 2) conifer wood surface in air at 10 kV for 10 min.

particles resulting from accumulation of surface oxygen–containing groups during the corona treatment. A comparative ESCA analysis of nontreated and corona-treated conifer wood was made to confirm this suggestion.

ESCA

In Figure 4 the detailed C(1s) and O(1s) ESCA spectra of nontreated (curves 1) and of corona-treated conifer wood plates at 10 kV for 10 min (curves 2) are shown. An increase of C2 (from hydroxyl and ether groups) and a shoulder from the side of the chemical shifts of ═CO (C3) and –COOH (C4) groups in the C(1s) peak may be observed. At the same time, the O(1s) peak demonstrates some brightening and increase of intensity. These peculiarities indicate the formation of an additional amount of –OH groups (there are also such groups on the surface of the nontreated sample) and oxygen-containing groups like –COOH that fail to accumulate on the surface of the nontreated sample. The accumulation of surface polar groups (–OH, –COO, ═CO) probably contributes to the increased level of interaction at the wood flour particles/rubber matrix interface and thus to the improvement of the mechanical parameters of the vulcanizates. Increasing the hydrophilicity of the wood flour particles leads to a slight increase of the water adsorption.

CONCLUSIONS

Corona treatment of wood flour under optimal operating conditions offers the possibility of improving its efficiency as a filler for rubber compounds. The modulus M_{300} and the tensile strength σ increase by about 46 and 60%, respectively, simultaneously with an increase of the elongation at break, when nontreated conifer wood flour is replaced by the same amount (50 phr/100 phr NBR) of plasma-treated wood flour at 10 kV for 10 min.

The effect of the wood flour corona treatment increases with the increase of its duration and voltage. The wood flour surface modification by treatment in cold oxygen plasma obtained in a corona discharge under optimal operating conditions turns the wood flour into a semiactive filler for NBR compounds.

Both the surface etching that changes the geometric area of the wood flour particles and the accumulation of surface oxygen-containing groups that changes the surface polarity of the wood flour particles explain the observed improvement of the mechanical properties attributed to improvement of the interaction at the wood flour particles/rubber matrix interface.

References

1. Vladkova, T.; Vassileva, St.; Natov, M. J Appl Polym Sci, to appear.
2. Domininghaus., H. Kunstoffe Gummi Kunstst 1979, 32, 295.
3. Kolupaev, B. S.; Demianiuk, B. P.; Êoëöïàåâ, Á. C. Sb. Struktura I Mekhanicheskie Svojstva Visokomolekulyarnikh Soedinenij; Ed. Naukovaya Dumka: Kiev, 1976; p. 87.
4. Natov, M.; Vassileva, St.; et al. Eur. Pat. 953 EP/16, 1987.
5. Videlov, Ch. Zastita i Modifitsirane na Darvesinata; Ed. Martilen: Sofia, Bulgaria, 1993.
6. Quanying, Y. Chem Ind Forest Prod 1996, 16, 75.
7. Flink, P.; Stenberg, B. Br Polym J 1990, 22, 147.
8. Ahlblad, G.; Kron, A.; Stenberg, B. Polym Int 1994, 33, 103.
9. Ahlblad, G.; Reitberger, T.; Stenberg, B.; Danielsson, P. Polym Int 1996, 39, 261.
10. Andrzej, K.; Bledzki, J. G.; Lucka, M. Polymery 2000, N2, 45.
11. Marcovich, N. E.; Aranguren, M. I.; Reboredo, M. M. Polymer 2001, 42, 815.
12. Alma, M. H.; Shirashi, N. J Polym Eng 1998, 18, 179.
13. Blithe, A. R.; Briggs, D.; Kendall, C. R.; Rance, D. G.; Zichi, V. J. Polymer 1978, 19, 1273.
14. Dineff, P. Electrotechnologiya; TUS: Sofia, Bulgaria, 2000.
15. Galinov, J. F.; Dubinina, G. G.; Masagutov, R. M. Metodi analiza katalizatorov neftepererabotki; Himiya: Moscow, 1973.
16. Gelius, U.; Heden, P.; Hedman, J.; Lindberg, B.; Nordlinf, C.; Siegban, K. Phys Scr 1970, 2, 70.
17. Scofild, J. H. J Electron Spectrosc Relat Phenom 1976, 8, 129.