Wood Flour: New Filler for the Rubber Processing Industry. IV. Cure Characteristics and Mechanical Properties of Natural Rubber Compounds Filled by Non-Modified or Corona Treated Wood Flour

T. G. Vladkova,[1] P. D. Dineff,[2] D. N. Gospodinova,[2] I. Avramova[1]

[1]*Department of Polymer Engineering, University of Chemical Technology and Metallurgy, Sofia, Bulgaria*
[2]*Department of Electrical Apparatus and Technology, Technical University, Sofia, Bulgaria*

Received 9 April 2005; accepted 30 August 2005
DOI 10.1002/app.23730
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: It is presented here how some cure characteristics and mechanical properties of rubber compounds based on nonpolar rubber, natural rubber (NR), are affected by filling with conifer wood flour, both nonmodified or corona treated in air or in ammonia. The corona treatment was performed at room temperature and varied both: treatment duration and voltage to find out the maximal reinforcing effect of the modified wood flour. The discharge voltage was varied at 10, 12, and 15 kV to include both (1) the range of relative low voltages (lower than 10 ÷ 12 kV in which the major active species arise from ionized and activated air oxygen and (2) the range of relative high voltages (12 kV and higher) in which the active species arise from simultaneously ionized and activated air oxygen and nitrogen. The chemical composition of the nonmodified and corona-treated wood surface was controlled by X-ray photoelectron spectroscopy (XPS) analysis. The activity of the modified wood flour was evaluated by comparative measurement of some basic mechanical parameters of rubber compounds, filled at equal level by nonmodified or plasma-treated wood flour. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 651–658, 2006

Key words: conifer wood flour; nonmodified and activated through corona treatment in air or in ammonia; XPS analysis; filled NR compounds; cure characteristics; mechanical properties; ageing resistance

INTRODUCTION

The wood is a renewable natural material and the waste wood is an important biomass resource. Many research groups are looking for ways to its utilization including new polymer composites development. There are a number of publications discussing possible wood filler modifications aimed at improvement of some technological and exploitation properties of such composite materials. Surprisingly, there is scant information about rubber compounds filled by wood-based disperse or fibrous fillers, although they hide interesting potential applications.

Utilization of wood floor, made by conventional grinding of amortized railway traverses, as a filler in thermosetting epoxy resin/rubber compounds for high quality traverses production has been described in ref. 1. Nagay and Erman[2] have investigated the reinforcing effect of a hybrid carbon black/mica filler in both acrylonitrile–butadiene rubber (NBR) and NBR/polyvinylchloride (PVC) compounds. The effect of the mica replacement by wood flour on the mechanical properties, swelling, and cure behavior of the corresponding composites has been discussed in this article. Ismail and Nurdin[3] studied the tensile properties of oil palm wood flour/natural rubber composites and also performed scanning electron microscopy observations of fracture surfaces of these composites. They have found that the tensile modulus increases with the increase of the oil palm wood flour concentration whereas the tensile strength and the elongation at break show an opposite trend. The improvement of the oil palm wood flour/rubber matrix interface interaction by different bonding agents has been substantiated with scanning electron microscopy. But systematic investigations on the effect of wood flour in rubber as well as in rubber/plastic compounds are missing. Our preliminary experiments showed the excellent wood flour ability to mix with all widely used rubbers: natural rubber, isoprene rubber, styrene rubber, butadiene rubber, acrylonitrile–butadiene rubber, etc. It has been found that the nonmodified wood flour acts as nonactive filler to NBR and NBR/PVC compounds[4] and corona treatment in air under optimal

Correspondence to: T. G. Vladkova (TGV@uctm.edu).
Contract grant sponsor: National Science Fund of Bulgaria; contract grant number: 1301/03.

operation conditions turns it into semiactive filler to NBR.[5] The addition of phenol-formaldehyde resin, acting as a compatibilizer in such compounds leads to an additional improvement of the mechanical properties and ageing resistance.[6]

It is well known that the reinforcing effect of the fillers depends on a lot of factors and the reinforcing mechanism is quite complicated. It is difficult to predict the effect of the same filler in compounds based on polymers with different polarity, physical properties, and chemical nature and containing other ingredients. To study more, in detail, the effect of the wood flour in rubber compounds, we continue our investigation employing other rubber matrices. This announcement is concerning the effect of nonmodified and corona treated (both in air and in ammonia) conifer wood flour in rubber compounds based on a nonpolar rubber, namely natural rubber (NR). It is demonstrated here how the wood flour surface composition is affected by the corona treatment under the chosen operation conditions (by XPS analysis) and how it reflects on the cure characteristics, same basic mechanical properties, and ageing resistance of the respective wood flour filled NR compounds.

EXPERIMENTAL

Natural rubber, SMR5 (Malaysia) and conifer wood flour, manufactured by firm "Maritsa," Kostenets, Bulgaria, with parameters according to Bulgarian standard 3718–74, particles' size lower than 140 μm and humidity of $\sim$6%, were used in our investigation.

The model rubber compounds contained traditional ingredients (phr): NR (SMR5), 100; wood flour, nonmodified, varied 0–70 or corona treated, 40; stearic acid, 2; zinc oxide, 3; sulfur, 2; and sulfenamide accelerator (Vulkacit CZ, Bayer), 2. All the materials used were of standard rubber industry grade and not purified for this study.

The modified wood flour was prepared by corona treatment in air or in ammonia under the following conditions: thickness of the wood flour layer, 4 mm; voltage, 10, 12, or 15 kV; duration, 1, 3, 5, or 10 min. Two characteristic regions of the active cold plasma obtained in corona discharge were found in a former investigation[7]: (1) a region of relative low voltages (10–12 kV and lower) in which the polymer surface modification is mainly due to an interaction with ionized and activated air oxygen and (2) range of relative high voltages ($\sim$12 kV and higher) in which the surface modification is caused by the action of simultaneously ionized and activated air oxygen and nitrogen. Therefore, to study the modifying effect of the different active species onto the wood flour, corona treatment at 10, 12, and 15 kV was performed.

The model mixtures were prepared on laboratory roll mill with a friction ratio of 1 : 1.4, in a conventional way. The vulcanization characteristics were determined according to Bulgarian standard 15754–83 with Monsanto Rheometer model M100 at a temperature of 150°C. The vulcanization was carried out at this same temperature and the optimum cure time. The mechanical parameters were determined according to ISO/R37 (with standard mechanical parameters deviations of $\pm$10%) and the accelerated heat ageing –according to ISO/188.

XPS analysis was performed on polished conifer wood plates ($10 \times 10 \times 3$ mm^3) using an ESCALAB II MK VG Scientific spectrometer (AlK_α, excitation energy: 1486.6 eV) Complete spectral scans and detailed recordings of the main peaks were made at 10^{-8} Pa. The binding energy scale was fixed by assigning $E_B = 285$ eV to the —CH_2— carbon C1s-peak.

RESULTS AND DISCUSSION

Cure characteristics

The cure characteristics of NR compounds containing different amounts of nonmodified wood flour (mixtures 1–7) or constant amount of wood flour (40 phr/100 phr NR) corona treated in air (mixtures 8–10) or in ammonia (mix 10) under varied operation conditions are represented in Table I. The conventional increase of $M_{\min}$, $M_{\max}$, and ΔM with the increase of the filling level is evident for the mixtures 2–7. The scorch time, τ_{s1} of the same mixtures (mixtures 2–7) does not change significantly: it is of 3 : 10–4 : 00 min : sec including also the nonfilled one (mixture 1). It is evident also that in contrary to the mineral fillers, delaying significantly the vulcanization process, the nonmodified wood flour does not do it: the optimum cure time, τ_{90} (6 : 00–5 : 20 min : sec) of all NR compounds filled by 10–70 phr nonmodified wood flour/100 phr rubber (mixtures 2–7) demonstrates even a tendency to slight decreases as compared to that of the nonfiled compound (mix 1) having an optimum cure time, τ_{90} of 7 : 50 min : sec.

The cure characteristics of the mixtures 8–10, filled by 40 phr wood flour corona treated in air at 10, 12, or 15 kV, respectively, or in ammonia at 15 kV (mixture 11) as compared to these of the mixture filled by the same amount (40 phr) but nonmodified wood flour (mix 5) show the following: all five parameters $M_{\min}$, $M_{\max}$, ΔM, τ_{s1}, and τ_{90} are almost equal for the mixtures filled by 40 phr nonmodified (mix 5) or corona treated in air at 10 kV wood flour (mix 8). When the corona treatment in air was at higher voltages, i.e., 12 and 15 kV (mixtures 9 and 10), where modifying effect due to simultaneous activation of air oxygen and nitrogen was expected, $M_{\max}$ and ΔM increase and τ_{90} decreases slightly whereas $M_{\min}$ and τ_{s1} stay almost constant. The changes of the cure characteristics of the filled compounds are most pronounced when wood

TABLE I
Cure Characteristics of NR Compounds Filled by Nonmodified or Corona Treated Wood Flour

Mix No	Wood flour, phr/100 phr NR	M_{min}, dNm	M_{max}, dNm	ΔM, dNm	τ_{s1}, min;sec	τ_{90}, min:sec
	Non-modified					
1	0	1.5	26.0	24.5	4:00	7:50
2	10	2.2	36.0	33.8	4:10	6:00
3	20	2.4	36.9	34.5	3:10	5:50
4	30	2.6	41.6	39.0	3:40	5:40
5	40	3.0	45.0	42.0	3:20	5:20
6	50	4.0	53.5	49.5	3:10	5:30
7	70	4.2	62.5	58.3	3:50	5:30
	Constant amount of WF: (40 phr/100 phr NR) corona treated in air					
8	At 10 kV for 5 min.;	3.1	46.2	43.1	3:30	5:20
9	At 12 kV for 5 min;	3.0	48.2	45.2	3:40	5:00
10	At 15 kV for 3 min.	3.3	50.0	46.7	3:30	4:40
	WF (40phr/100phr NR) corona treated in ammonia,					
11	At 15 kV for 1 min	3.2	56.9	53.7	3:20	4:00

flour corona treated in ammonia (mix 11) instead of wood flour corona treated in air (mixtures 8–10) or nonmodified (mix 5) is used.

Mechanical properties, ageing

The mechanical parameters: modulus, M_{200} (curve 1), tensile strength,σ (curve 2), elongation at break,ε (curve 3), and Shore hardness (curve 4) of the non-modified wood flour filled NR vulcanizates are shown in Figure 1. It is evident that all these parameters are sensitive to the filling level: the Shore hardness (curve 4) increase with the increase of the filling level, as could be expected; the modulus M_{200} (curve 1) is almost constant in the region of the relative low filling level, (below 30 phr), in the region of 30–60 phr increases sharply and after that stays almost constant at the reached high level; the tensile strength, σ (curve 2) and the elongation at break, ε (curve 3) demonstrate an increase (much more better expressed at the tensile strength) in the region of low filling level (below 40 phr/100 phr NR) where the modulus M_{200} is relatively low. Having for that the NR is a crystallizing polymer, such dependence of the tensile strength, σ on the filling level is not surprising and it is good explained by the theory of superhigh strained macromolecules.[8,9]

It was proven in a previous investigation[5] that corona treatment in air changes the surface chemical composition, porosity, and the surface roughness of conifer wood flour. It was demonstrated also that these changes reflect on the mechanical parameters of the filled NBR and turn the wood flour into semiactive filler to this polar rubber. On the basis of the expectation that the corona treatment would influence somehow the mechanical parameters of other filled elastomers, experiments with nonpolar rubber, namely NR were performed. The mechanical parameters of the NR compounds filled by constant amount (40 phr/100 phr NR) corona treated in air (at 10, 12, or 15 kV for 1, 3, 5, or 10 min) wood flour are represented in Figure 2. It appeared that the Shore hardness of all compounds filled by 40 phr wood flour (nonmodified or corona treated under the chosen conditions)/100 phr, NR is 70–75, i.e., almost equal and therefore any data about this parameter are shown in Figure 2. The other mechanical parameters: modulus M_{200} (curves 1, 1′, 1″), tensile strength, σ (curves 2, 2′, 2″) and elongation at break, ε (3, 3′, 3″) are influenced by the corona treatment of the filler in the manner shown by the corresponding curves in the Figure 2. It is evident that the effect of the corona-treated wood flour depends on both the voltage and the treatment duration. The three mechanical parameters: modulus $M_{200,}$ tensile strength, σ, and elongation at break, ε, reach their maximal values when the corona treatment in air is for 5 min at 10 or 12 kV and for 3 min at 15 kV. In the last case (corona treatment at 15 kV), the modulus M_{200} (curve 1″) increases with about 42%; the tensile strength, σ (curve 2″), with about 27% and the elongation at break, ε (curve 3″), with about 30% as compared to the corresponding parameter of the NR compound filled with the same amount of nonmodified wood flour.

The increase of the mechanical parameters is better expressed at the NR compounds filled with corona-treated wood flour at 15 kV, i.e., at voltage at which nitrogen containing groups accumulation on the wood flour surface was expected. This result gave us reason to try to increase additionally the concentration of nitrogen containing groups on the wood flour surface performing the corona treatment in ammonia instead

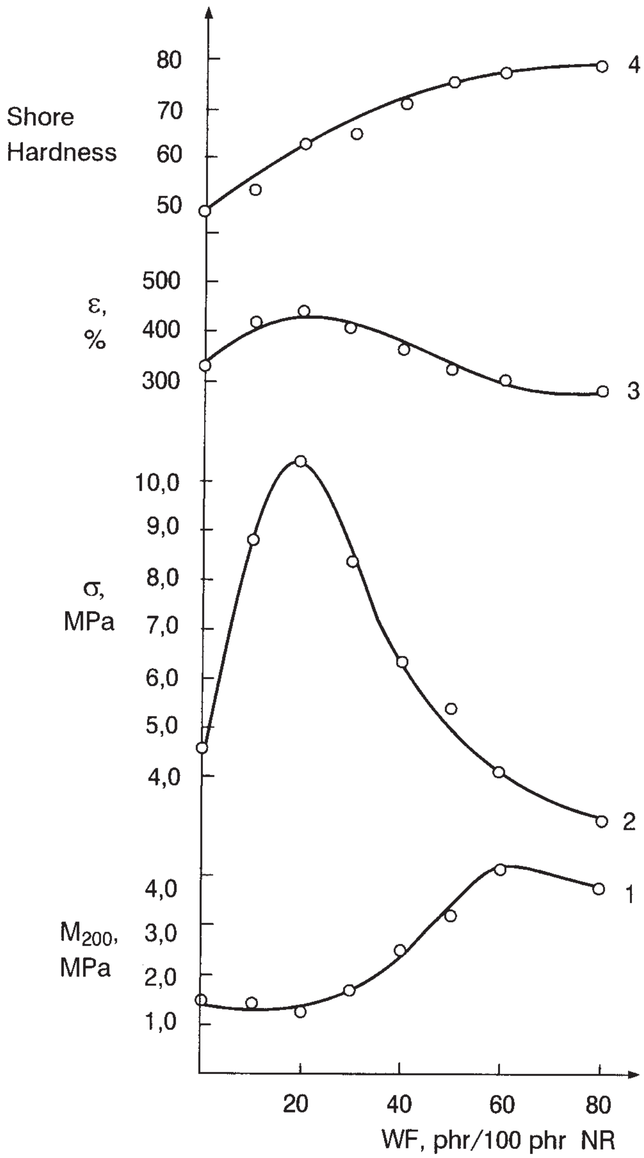

Figure 1 Dependence of the mechanical properties: modulus M_{200} (curve 1), tensile strength, σ (curve 2), elongation at break, ε (curve 3), and Shore hardness (curve 4) of NR vulcanizates on the filling level by nonmodified wood flour.

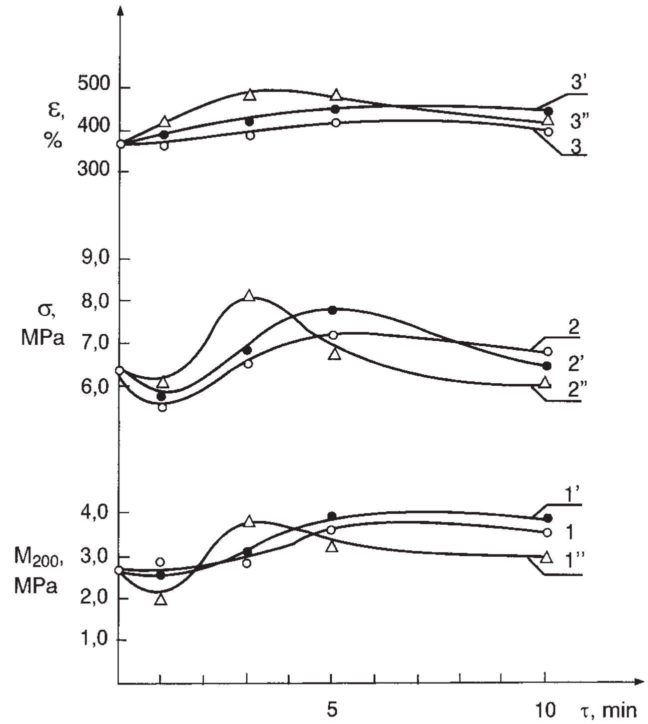

Figure 2 Mechanical properties: modulus M_{200} (curves 1, 1′, 1″), tensile strength, σ (curves 2, 2′, 2″), and elongation at break, ε (curves 3, 3′, 3″) of NR vulcanizates filled by 40 phr/100 phr rubber nonmodified or corona treated for 1, 3, 5, or 10 min in air at 10 kV (curves 1, 2, 3); 12 kV (curves 1′, 2′, 3′), and 15 kV (curves 1″, 2″, 3″) wood flour.

of air medium. The mechanical parameters of NR compounds filled with corona treated in ammonia (instead of corona treated in air) wood flour (40 phr/100 phr NR) are represented in the next Figure 3. It is evident that the corona treatment in ammonia for short time (1 min) at 15 kV leads to the most pronounced changes of the mechanical parameters: the tensile strength, σ, and elongation at break, ε, increase with about 48 and 35%, respectively, and the modulus M_{200} decreases simultaneously with about 30% as compared to these of the NR compound filled with the same amount nonmodified wood flour. The Shore hardness is not sensitive on such modification and therefore data about this parameter are not shown

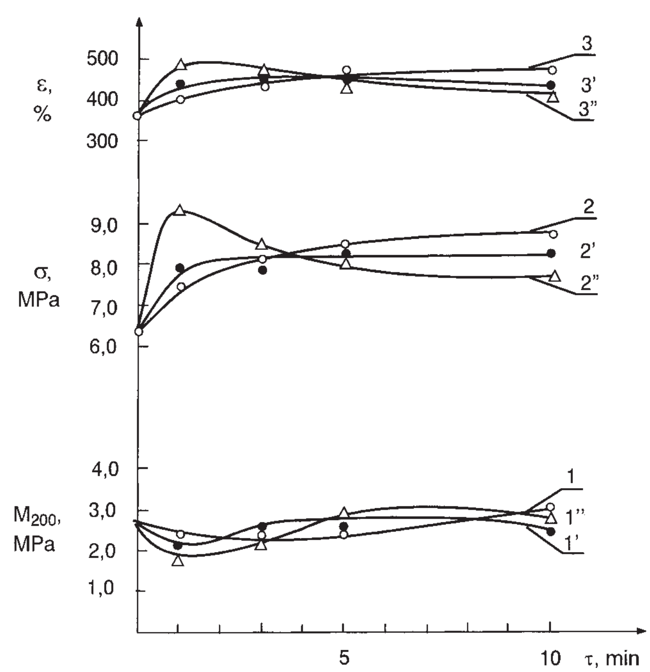

Figure 3 Mechanical properties: modulus M_{200} (curves 1, 1′, 1″), tensile strength, σ (curves 2, 2′, 2″), and elongation at break, ε (curves 3, 3′, 3″) of NR vulcanizates filled by 40 phr/100 phr rubber nonmodified or corona treated for 1, 3, 5, or 10 min in ammonia at 10 kV (curves 1, 2, 3); 12 kV (curves 1′, 2′, 3′), and 15 kV (curves 1″, 2″, 3″) wood flour.

TABLE II
Percent Change of the Mechanical Parameters of NR Compounds Filled by Nonmodified or Corona Treated Wood Flour after Ageing at 70°C for 168 h

Mix No	Wood flour, phr/100 phr NR	ΔM_{200} (%)	$\Delta\sigma$ (%)	$\Delta\varepsilon$ (%)	Δ Shore hardness, units
	Non-modified				
1	0	0	−40.9	−39.6	+16
2	10	+2.2	+6.9	−30.8	+1
3	20	0	−36.9	−32.5	+8
4	30	+2.6	−40.6	−30.0	+6
5	40	+30.8	−30.8	−22.5	0
6	50	−9.6	−41.9	−35.1	0
7	70	+4.2	+12.5	−18.3	+2
8	Constant amount of WF: 40 phr/100 phr NR corona treated in air				
9	At 10 kV for 5 min.;	+6.3	+1.9	−21.0	+1
10	At 12 kV for 5 min;	−1.0	−21.0	+3.0	+3
	At 15 kV for 3 min.				
11	WF 40phr/100phr NR corona treated in ammonia				
	At 15 kV for 1 min	0	−6.9	−13.7	+2

here. A comparison of curves in Figure 2 to these in Figure 3 indicates that the maximal modifying effect of the corona treatment in ammonia is achieved at 15 kV for 1 min, whereas of the corona treatment in air at the same voltage (15 kV) is achieved for 3 min.

The aging resistance of the studied NR filled with wood flour (nonmodified or corona treated in air or in ammonia) NR compounds was evaluated by the percent change of three mechanical parameters: tensile strength, σ, elongation at break, ε, and Shore hardness after ageing in air at 70°C for 168 h, and the results are represented in Table II. No clearly expressed dependence of the aging resistance on the filling level is observed but is evident that the filling of NR by wood

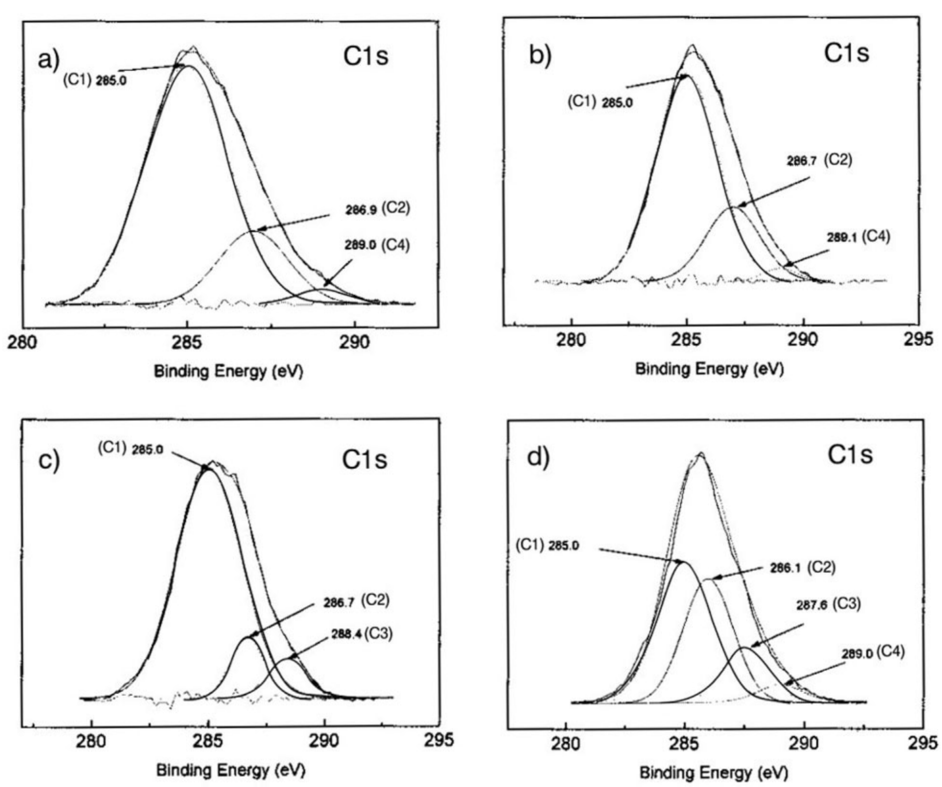

Figure 4 Detailed C1s XPS peaks of conifer wood surface: nonmodified (a); corona treated in air at 10 kV for 5 min (b); corona treated in air at 15 kV for 3 min (c); and corona treated in ammonia at 15 kV for 1 min (d).

flour does not worse this parameter (compare samples 2–7 with sample 1). A comparison of samples 8–10 and 11 to sample 1 demonstrates that that corona treatment of wood flour in air or in ammonia does not degrade the aging resistance of the filled NR vulcanizates. In opposite, a tendency to bettering is observed when the wood flour is corona treated in ammonia: the percent changes of the tensile strength, $\Delta\sigma$, elongation at break, $\Delta\varepsilon$, and Shore hardness of mix 11 containing 40 phr corona treated in ammonia wood flour/100 phr rubber are less pronounced as compared to these of mixture 5 containing the same amount nonmodified wood flour.

The reinforcing effect of corona treated conifer wood flour in NBR compounds, earlier observed by us,[5] was attributed to both (1) the increased surface roughness of its particles increasing the wood flour/rubber matrix interface contact area and the mechanical bonding due to a more dept diffusion of the rubber within the wood particles volume and (2) the surface oxygen containing groups accumulation, increasing the polarity of the wood surface, and the compatibility with the polar rubber matrix.

NR is nonpolar rubber and one could expect opposite influence of these both factors, namely: the increased wood flour surface roughness to support the mechanical bonding and the surface enrichment of polar groups to worse the interaction with the nonpolar rubber matrix. The predominance of one of these both factors may determine the direction of the mechanical parameters change. In addition, the direction and degree of this change could be influenced by other chemical and physical interactions in the compounds during the vulcanization, etc. To obtain more detailed information about the surface chemical composition of the employed in this case wood flour, corona treated in air or in ammonia under the chosen operation conditions, comparative XPS analysis of nonmodified and corona treated conifer wood samples was performed.

XPS analysis

It is well recognized that corona treatment in air produces surface oxidation of polymers.[10] Corona discharged free radicals, electrons, ions, excited neutrals, and photons interact with polymer surfaces to form radicals, reacting rapidly with atmospheric oxygen. Such reactions lead to functionalization and crosslinking of the polymer surface. The peroxide groups decomposition produces C—OH, C═O and O═C—O groups, that have been identified by XPS,[11,12] To study the possible changes in the wood surface composition due to the corona treatment, comparative XPS analyses of nonmodified and corona treated conifer wood was performed expecting that it could explain to some extent the observed improvement of some mechanical parameters of some filled NR compounds.

Carbon C1s and oxygen O1s were detected on the wide scan XPS spectra (i.e., survey spectra) of all investigated surfaces together with nitrogen N1s on the surfaces, corona treated in air at relative high voltage, 12 and 15 kV as well as on the corona treated one in ammonia. The surfaces also contain hydrogen, but this element is not detectable by XPS.

The ratio of the elements was calculated from the curve area under each detailed peak of the corresponding detected element by using the atomic sensitivity factor[13]: σ(C1s) = 1.00, σ(O1s) = 2.93, and σ(N1s) = 1.68. This allowed expressing of the surface chemical composition by atomic percent of the elements, which indicates the relative concentration of each element. The components of the carbon and oxygen atoms were determined from the deconvoluted spectra by a computer curve fitting and determining of the binding energy shifts for C1s and O1s.

The curve fit carbon C1s peak of the nonmodified [Fig. 4(a)] and corona-treated wood flour in air at relative low voltage, 10 kV [Fig. 4(b)], comprised three main components: C1, C2, and C4 whereas that of the corona-treated wood flour in air at relative high voltage, 12 or 15 kV [Fig. 4(c)] comprised also three main components but the third one was C3 instead of C4, that indicates existence of different types O bonding to carbon, C, in these cases. The curve fit carbon C1s peak of the corona-treated wood flour in ammonia [Fig. 4 (d)] comprised all four components: C1, C2, C3, and C4 indicating the existence of the all types oxygen to carbon bonding on the treated wood surface, i.e., its more complicated chemical compound. The curve fit oxygen O1s peak of all wood samples, nonmodified and corona treated, was comprised of O1 and O2 components, related to the carbon C1s components: the O1 component, centered at 531.8 eV related to C3 and C4 type of carbon in C═O bonds and O2 component, centered at 532.9 eV, connected with C2 type carbon as C—O bonds.

According to the literature,[14–21] the C1 component centered at 285 $\pm$ 0.4 eV arises form carbon atoms bounded only to other carbon or hydrogen atoms. The C2 component at 286.5 $\pm$ 0.4 eV arises from carbon atoms bounded to a single noncarbonyl oxygen atom in addition to another carbon or hydrogen atom. The C3 component represents carbon atoms bonded to another carbon and hydrogen atoms, plus either (1) one carbonyl oxygen atom, or (2) two noncarbonyl oxygen atoms. The C4 component is carbon linked to carbonyl and noncarbonyl oxygen. The O1 component of O1s peak, centered at 531.8 $\pm$ 0.4 eV and the O2 component of O1s centered at 532.9 $\pm$ 0.4 eV represent oxygen atoms bonded to carbon: C═O and C—O, respectively.

The atomic percents of the detected elements, carbon, oxygen, and nitrogen, are shown in Table III. The observed changes in atomic percents according to the

TABLE III
Atomic Composition as Derived from XPS Analysis of Nonmodified and Corona Treated in Air or in Ammonia Wood Samples

Mix No	Sample	C1s atom (%)	O1s atom (%)	N1s atom (%)	O1s/C1s	C1s Components C1, area (%)	C2, area (%)	C3, area (%)	C4, area (%)
5	Wood flour, non modified	70.6	29.4	—	0.42	76.9 (285.0eV)	19.5 (286.9eV)	3.6 (289.0eV)	—
	Wood flour, corona treated in air								
8	At 10 kV for 5 min.;	68.8	30.8	—	0.48	74.3 (285.0eV)	23.3 (286.9eV)	2.5 (289.1eV)	—
9	At 12 kV for 5 min.	65.6	34.0	0.4	0.52	76.2 (285.2eV)	19.2 (286.9eV)	—	4.6 (288.2eV)
10	At 15 kV for 3 min.	64.4	35.0	0.6	0.54	81.0 (285.0eV)	10.9 (286.7eV)	—	8.1 (288.4eV)
	Wood flour, corona treated in ammonia								
11	At 15 kV for 1 min	73.9	25.2	0.9	0.34	45.7 (285.0eV)	34.6 (286.1eV)	5.4 (289.0eV)	14.3 (287.6eV)

Carbon types	bonding	binding energy (eV)
C1:	C-C or C-H	285.0 ± 0.4
C2:	C-O	286.5 ± 0.4
C3:	C=O or O-C-O	288.0 ± 0.4
C4:	O-C=O	289.0 ± 0.4

C1s, O1s, and N1s peak areas, show that the corona treatment affects significantly the chemical composition of the conifer wood surface and the changes are deeper when the treatment is performed at higher voltages and in ammonia medium (compare samples 8–11 to sample 1; samples 8–10 to sample 11).

The percent of the oxygen increases and consequently, the percent of the carbon decreases when the treatment is performed in air at relative low voltage, 10 kV (sample 8) and the atomic O/C ratio for the nonmodified wood of 0.42 (sample 1) get up to 0.48 for the corona-treated sample (sample 8). Small percents of nitrogen, together with the carbon and oxygen, are detected for the corona-treated wood samples in air at relative high voltages, 12 and 15 kV (samples 9 and 10). This confirms our presumption that nitrogen-containing groups could be accumulated when the corona treatment in air is at relative high voltages, approximately 12 kV and higher, at which air nitrogen is activated together with the oxygen.

For the wood samples, corona treated in air, both at 12 and at 15 kV, the O/C atomic ratio is higher, of 0.52 and 0.54, respectively, (samples 9 and 10) compared to that of the nonmodified wood flour of 0.42 (sample 1), indicating that at these voltages simultaneously with the nitrogen containing groups accumulation run surface oxidation. It is interesting also that the C4 instead of the C3 carbon component appears for these samples 9 and 10. Evidently, the oxidation process is altered somehow when in the plasma present nitrogen together with oxygen active spaces and the altered type of the oxygen to carbon bonding is due to this.

The largest seems to be the changes in the surface chemical composition of the wood sample corona treated in ammonia (sample 11): its N1s atomic percent is higher compared to that of the samples, corona treated in air at relative high voltages (samples 9 and 10) indicating that the corona treatment in ammonia instead of in air leads to the expected enrichment of the wood surface by nitrogen containing groups; its O/C ratio is lower compared to that of the other corona treated samples (samples 8–10) and could be accepted as an evidence for oxidation process suppressing; its O/C ratio is lower compared also to that of the nonmodified wood sample (sample 1) and its C1s peak contains all four components:C1, C2, C3, and C4, indicating the presence of all types oxygen to carbon bonding. It is clear that the corona treatment in ammonia leads to a drastic surface chemical composition altering. The wood surface modification under these conditions is complicated and needs in separate, a more detailed study. This is a topic of further investigation, including other nitrogen-containing modifying agents like, diaminocyclohexane. Anyway, the results of this XPS analysis confirm that the corona treatment in air at relative high voltages, 12 kV and higher, offer a possibility to introduce together with oxygen also nitrogen containing groups on the conifer wood flour surface and the NR compounds filled by such modified wood flour demonstrate slightly higher mechanical parameters compared to the vulcanizate filled by the same amount wood flour corona treated in air at lower voltage, namely 10 kV, that does not contain nitrogen (Fig. 2, curves 1′,1′, 2′,2′, and 3′,3″ compared to curves 1,2,3). The corona treatment in ammonia at 15 kV suppresses surface oxidation and additional increases the nitrogen content on the wood surface. The filled by such modified wood flour NR compound demonstrate the highest tensile strength (Fig. 3, curve 2″) and ageing resistance (Table II, sample 11). The positive changes observed at the mechanical parameters of NR compounds filled by modified wood flour with surface grafted nitrogen containing groups thorough corona treatment in air at relative high voltages or in ammonia, could be due to their participation somehow in the vulcanization process. The last one is indicated by the changes observed at the vulcanization characteristics (Table I, compare mixtures 11 and 10, 9 to mixture 5, all filled by equal amount wood flour: corona treated in ammonia[11] or in air[10,9] or nonmodified).

CONCLUSIONS

Nonmodified wood flour does not delay the vulcanization of the filled natural rubber compounds. The basic mechanical parameters of their vulcanizates depend significantly on the filling level. A sharp increase of the tensile strength, σ, accompanied with a slight increase of the elongation at break, ε, and Shore hardness are observed in the range below 30–40 phr wood flour/100 phr NR.

Corona treatment under optimal operation conditions offers a possibility to increase the efficiency of wood flour as filler to NR compounds. Corona treatment in ammonia, as compared to the corona treatment in air, is more effective tool to increase the wood flour reinforcing effect in nonpolar rubbers: shorter time (1 min in ammonia and 3 min in air at equal voltage, 15 kV) is necessary to reach an optimal (regarding the mechanical parameters) wood flour surface composition and the tensile strength, σ, and elongation at break,ε, of the filled NR compounds are slightly higher. The replacement of 40 phr nonmodified by the same amount corona treated in ammonia wood flour increases the tensile strength with about 48% and the elongation at break with about 35%.

Corona treatment in ammonia causes more complicated altering of the wood surface chemical composition due to suppressing of the surface oxidation and an accumulation of nitrogen containing groups. Such treatment is to be preferable regarding the reinforcing effect of conifer wood flour in nonpolar rubbers.

References

1. Schulte, S.; Kern, H. German Pat. 3,345,858 (1985).
2. Nagay, N.; Erdman B. Presented at the Proceedings of the International Symposium "EUROFILLERS' 99," September 6–9; Villeurbanne, France, 1999.
3. Ismail, H.; Nurdin, H. I. Iranian Polym J 1998, 7, 53.
4. Vladkova, T.; Vassileva St., Natov M. J Appl Polym Sci 2003, 90, 2734.
5. Vladkova, T.; Dineff, P.; Gospodinova, D. J Appl Polym Sci 2004, 91, 883.
6. Vladkova, T.; Dineff, P.; Gospodinova, D. J Appl Polym Sci 2004, 92, 95.
7. Dineff, P.; Boshnakova, R. Presented at the Proceedings of the IXth International Symposium, Electr. Apparatus and Technologies, "SIELA," Sofia, June 1–2, 2000; Vol. 1, p. 214.
8. Djagarova, E. Rubber Technology; Sofia: Art Grafic, 2000.
9. Katz, H. S., Milewski, J. V., Eds. Handbook of Fillers and Reinforcements for Plastics; Los Alamos Sci. Lab: New Mexico, 1981.
10. Chi-Ming Chan. Polymer Surface Modification and Characterization; SPE Books, Hanser Publishers: Munich, 1992.
11. Mora, M.; Occienco, E.; Garbassi, F. Surf Interface Anal 1990, 16, 911.
12. Clark, D. T., Feast, W. J., Eds. Polymer Surfaces Wiley: New York, 1978; p. 345.
13. Scofield, J. H. J Electron Spectrosc 1976, 8, 129.
14. Ahmed, A.; Adnot, A.; Kaliaguine, S. J Appl Polym Sci 1987, 34, 359.
15. Doris, G. M.; Gray, D. G. Cellulose Chem and Technol 1978, 12, 9.
16. Hua, X.; Kaliaguine, S.; Kokta, B. V.; Adnot, A. J Wood Sci and Technol 1993, 27, 449.
17. Kamdem, D. P.; Riedel, B.; Adnot, A.; Kaliaguine, S. J Appl Polym Sci 1901 1991, 43.
18. Koubaa, A.; Riedel, B.; Koran, Z. J Appl Polym Sci 1996, 61, 545.
19. Liu, F. P.; Rials, T. G. Langmuir 1998, 14, 536.
20. Ostmeyer, J. G.; Elder, T. J.; Littrell, D. M.; Tatarchuk, B. J.; Winandy, J. E. J Wood Sci and Technol 1988, 8, 413.
21. Sernek, M. Comparative Analysis of Inactivated Wood Surfaces, Doct. Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 2002.