Sulfur-Free Lignin as Reinforcing Component of Styrene–Butadiene Rubber

B. Košíková, A. Gregorová

Institute of Chemistry, Slovak Academy of Sciences, 845 38 Bratislava, Slovak Republic

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ABSTRACT: The potential application of lignin biopolymer as a component of styrene–butadiene rubber was examined with regard to its ability to reinforce the vulcanizates. It was shown that the sulfur-free lignin preparation improved physicomechanical properties of rubber. The determination of the coefficient of lignin activity confirmed that lignin acts as an active filler. FTIR characteristics of lignin isolated from the vulcanizate containing 20 phr lignin indicated its interaction with the sulfur system, resulting in formation of noncyclic sulfide structures. In the case of higher lignin amount in the vulcanizate, some interfacial interaction between lignin and SBR may occur. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 924–929, 2005

Key words: lignin; styrene–butadiene rubber; mechanical properties; vulcanization; FTIR

INTRODUCTION

It is well known that lignin is a polydisperse natural polymer consisting of phenylpropane (C_6–C_3) units and that some differences in its molecular mass and type of functional groups exist dependent on the genetic origin of the wood and the method of isolation. About 50 million tons of lignin per year is produced from the chemical treatment of wood at pulp mills. Lignin as an abundant and relatively low-priced substance has attracted great attention for its use in engineering plastics as phenolformaldehyde resins, polyurethane foams, etc.[1,2] These studies have illustrated that some lignin preparations can be incorporated into the matrix of polymeric materials and that the major limitation for the use of lignin in polymeric products concerns its polydisperse and multifunctional characteristics. In our previous papers,[3,4] the lignin biopolymers were found useful for the preparation of composite polyolefin films. It was shown that lignin modified the surface properties of polypropylene, resulting in an increase in its hydrophilicity.[5] Certain interactions of lignin with polypropylene during the processing of composite blends were confirmed in our previous paper by electron spin resonance spectroscopy.[6]

In the majority of applications the raw rubber is mixed with various ingredients to modify its characteristics. Recently, the mutual interaction between wood components and styrene–butadiene rubber (SBR) has been examined by measuring the dynamic mechanical properties of filled polymers.[7] The authors revealed that the fillers immobilize the polymer by adsorption on its surface. In the case of lignin the interaction could be explained by high lignin adsorption affinity to various compounds such as cholic acids and *N*-nitrosoamines described in our previous papers.[8,9] The use of lignins in elastomers is hampered by the structural complexity of lignin and its genetic variability. The main technical lignins derived from kraft and sulfite wood pulping were tested as a compounding ingredient in rubber. Applications of dry mill kraft lignin into SBR showed almost no reinforcing effect. Incorporation of this lignin into rubber by latex masterbatching increases reinforcing characteristics. However, they are very sensitive to precipitate temperature and particle size.[10] Sodium lignosulfonate powder isolated from sulfite spent liquor improved properties such as tear and abrasion resistance, but it has a negative effect on modulus, tensile strength, and resilience.[11] The objective of the present article was to examine the effect of sulfur-free lignin derived from beech wood prehydrolysis on the reinforcing characteristics of SBR.

EXPERIMENTAL PROCEDURES

Materials

Styrene–butadiene rubber KRALEX 1500 (styrene content 23% wt) purchased from Kaucuk Kralupy, Czech Republic was used as an elastomer in the model experiments. The vulcanization system was based on sulfur and sulfenamide accelerators. Powdered lignin of average molecular mass 2,000 and polydispersity 1.2 was obtained by fractionation of byproducts of

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Correspondence to: B. Košíková (chemkosi@savba.sk).

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TABLE I
Formulation of SBR Rubber Mixtures

Ingredient	[phr][a]
Kralex 1500	100
Lignin	0, 5, 10, 15, 20, 30, 40, 50, 60
Zinc oxide	5
Stearic acid	2
Sulfur vulcanization system[b]	8.5

[a] Parts per hundred rubber.
[b] Sulfur + DPG + CBS in an adequate ratio.

beech wood prehydrolysis (170°C, 1 h) at the Lignin Laboratory, Institute of Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia. Gel permeation chromatography was performed on a column (53 × 8 cm) of Sephadex LH 60 using a mixture of dioxane and water containing 0.005*M* NaOH and 0.001*M* LiCl (7 : 3) as the eluant.[12]

Preparation of blends and vulcanizates

The formulation of the prepared rubber blends is shown in Table I. The mixtures of dry lignin powder and rubber were prepared in a Brabender Plastograph kneader with 75-cm^3 chamber in two steps. Fill factor used in the mixing was 0.8. In the first step rubber was kneaded with ZnO and stearic acid at 80°C, 70 rpm during 1 min. Consequently lignin was added and kneaded with this compound for 5 min. This mixed stock was dumped and masticated to form a band on the calender Buzuluk rollers. The band of the first stage mixture was returned to the Brabender chamber and the sulfur vulcanization system was added. During the second stage the mixture was kneaded at 55°C, 70 rpm during 3 min. The mixed stock was dumped and finally sheeted off by calender Buzuluk.

Testing

Cure characteristics of the rubber compounds (scorch time t_{s2}, optimum cure time t_{90}, and torque increment ΔM) were determined according to STN 621416 using a Monsanto 100 rheometer at 150°C. Mooney viscosity was measured on a WPI Mooney viscometer at 100°C using a large rotor, a preheating time of 1 min, and a testing time of 4 min. The typical viscosity was reported as ML (1 + 4, 100°C). Vulcanized plates of 2 mm thickness were prepared by the vulcanization of blends using a hydraulic press at 150°C, 20 MPa for a time corresponding to the optimum of vulcanization of the individual blends. Test pieces for tensile tests were obtained by cutting the vulcanizates to obtain testing pieces type 1. Tensile strength at break, elongation at break, and stress at 100% elongation of vulcanizates were measured using a Monsanto 10 tensometer according to STN ISO 37 at 500 mm/min cross-head speed. The Shore A hardness of the vulcanizates was measured on testing equipment ZWICK according to STN ISO 7619. The coefficient of filler activity α_F was calculated according to Wolff.[13] The Tesla BS 300 scanning electron microscope was used for the observation of the cross-section of lignin SBR compound coated with gold.

The disintegrated vulcanizates containing 20 and 50 phr lignin were extracted with a mixture of ethanol–water, 3 : 1. The extraction was run until the solvent was colorless and then the obtained extract was evaporated under vacuum and dried under vacuum overnight. The yield of lignin fractions isolated from blends with 20 and 50 phr of lignin was 0.5 and 4.8% wt, respectively. The intense mechanical disintegration of vulcanizates allowed preparation of samples for Fourier-transformed infrared (FTIR) analysis. The FTIR spectra were measured in KBr pellets (2 mg sample/200 mg KBr) with a NICOLETMagna 750 spectrometer equipped with a DTGS detector. The spectra were acquired and manipulated with the use of Omnic (version 3.1) FTIR software at 4 cm^{-1} resolution and 128 scans.

RESULTS AND DISCUSSION

The used lignin sample was found to be dispersible in styrene–butadiene rubber by dry mixing. Figure 1 demonstrates the size and dispersion of lignin particles in elastomeric matrix, resulting in formation of a homogenic composite system. The average size of the dispersed spherical lignin particles is about 100 nm. The cure characteristics of lignin-free and lignin-containing SBR compounds are summarized in Table II. It

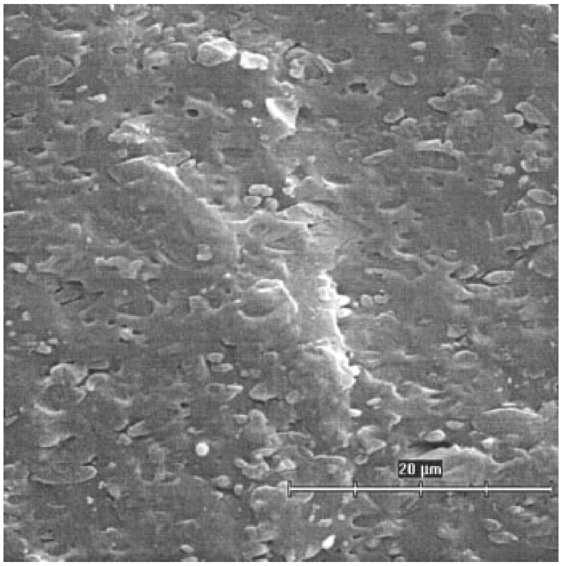

Figure 1 Scanning electron microscopy of SBR compounded with 50 phr lignin. Magnification ×5,000.

TABLE II
Vulcanization Characteristics of SBR Blends

Blend no.	Lignin content [phr]	Scorch time t_{s2} [min]	Optimum cure time t_{90} [min]	Torque increment ΔM [Nm]	Cure rate index [min^{-1}]
1	0	5.5	13.0	3.76	13.33
2	5	7.0	13.7	3.73	14.93
3	10	4.3	12.1	4.05	12.82
4	15	4.6	12.5	4.00	12.66
5	20	3.9	12.0	4.25	12.35
6	30	3.7	14.0	4.66	9.71
7	40	3.0	14.5	4.47	8.70
8	50	3.6	17.5	4.95	7.19
9	60	3.8	20.1	4.87	6.13

is evident that scorch time slowly decreased, whereas optimum cure time was almost constant up to 20 phr lignin and then increased significantly with the increasing lignin content in the rubber blends. These results indicate that lignin may affect the curing behavior, probably due to the interaction of lignin with the vulcanization system. The torque increment slightly increased and the cure rate index significantly decreased with lignin concentrations over 20 phr. To obtain more information about the lignin–rubber interaction, the coefficient of activity α_F was calculated according to the Wolff[13] pattern based on cure chatacteristics:

$$\frac{\Delta M_x}{\Delta M_0} - 1 = \alpha_F \frac{m_x}{m_p} \tag{1}$$

where m_x is the weight of lignin in the blend; m_p is the weight of rubber in the blend; ΔM_x is the increment of torque of the blend containing x phr of lignin; and ΔM_0 is the increment of torque of blend without lignin.

As is shown in Figure 2, the calculated coefficient of activity α_F achieved a positive value 0.6631 for the tested series of composite mixtures. This indicates that the lignin sample acts as an active filler, reinforcing the vulcanizates. Figure 3 shows that the Mooney viscosity of the SBR blend increases with the loading of lignin. It may be associated with the above calculated reinforcing ability of the used lignin sample. The effect of lignin on the mechanical properties of the prepared vulcanizates is illustrated in Figures 4–7. The properties such as stress at 100% elongation (Fig. 4), tensile strength at break (Fig. 5), and elongation at break (Fig. 6) improved remarkably with the increasing amount of lignin up to 50 phr. As shown on Figure 7, the hardness of the vulcanizates also increased with the increasing lignin concentration. The values ilustrated in Figures 4–7 indicate that optimum lignin concentration for maximum reinforcement is about 40 phr. The obtained results support the above-mentioned suggestion that lignin acts as a reinforcing agent for rubber. The reinforcing activity of the lignin preparation used in the SBR rubber blends in the amount from 20 to 50 phr can be connected with its low molecular weight and polydispersity. Reinforcement might be one of the functions of lignin in nature where lignin acts as a binder for cellulose fibers in

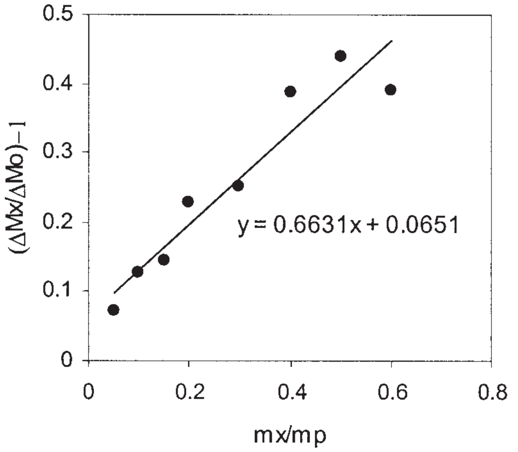

Figure 2 Coefficient of lignin activity α_F in SBR.

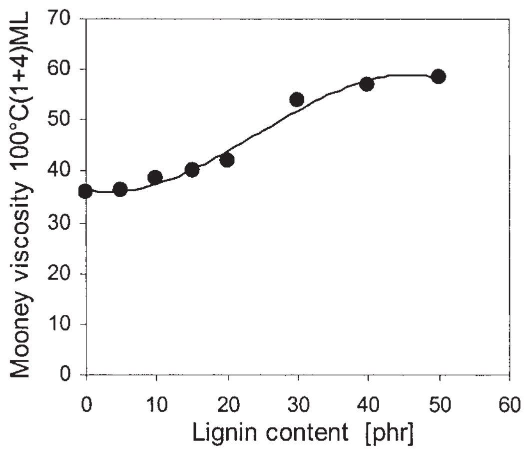

Figure 3 Dependence of Mooney viscosity on lignin content in rubber blends.

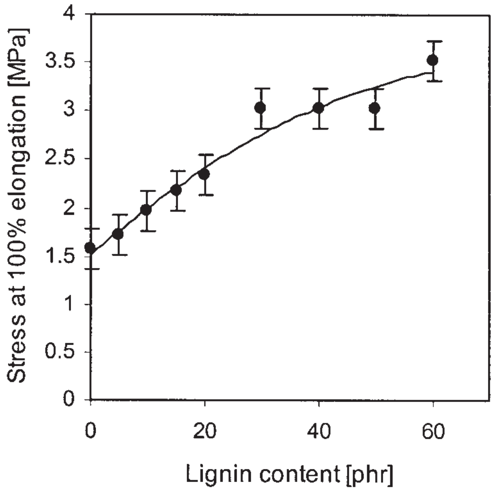

Figure 4 Effect of lignin content on stress at 100% elongation of vulcanizates.

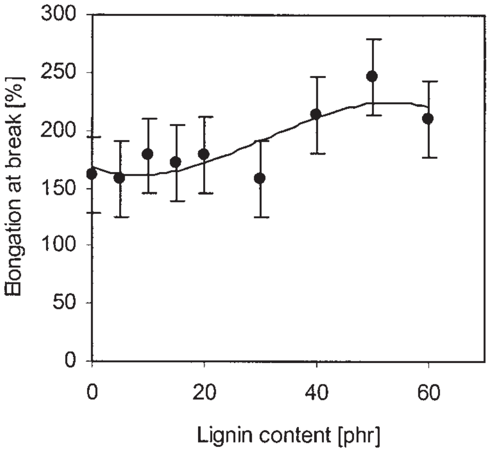

Figure 6 Effect of lignin content on elongation at break of vulcanizates.

wood and as a stabilizer against various stresses to which plants are exposed.

To explain this effect of lignin in the vulcanization of SBR, we have examined the structural changes of lignin by FTIR spectroscopy. The spectrum of the original lignin (Fig. 8) shows vibrations typical for beech wood lignin at 3400 cm^{-1} (OH), 2950–2850 cm^{-1} (CH), 1707 cm^{-1} (nonconjugated CO), 1610 and 1516 cm^{-1} (aromatic skeletal vibrations), 1460, 1425, and 1368 cm^{-1} (CH) corresponding to ring stretching CH in-plane deformation. The bands at 1327, 1272, and 1217 cm^{-1} belong to ring breathing with CO stretching. The two bands 912 and 831 cm^{-1} are assigned to the aromatic CH out-of-plane vibration, characteristic of syringyl nuclei. Comparison of the spectrum of the lignin fraction extracted from the SBR vulcanizate containing 20 phr of lignin with that of the original sample indicates a modification of the lignin macromolecule during vulcanization, resulting in demethylation, an increase in hydroxyl groups probably through ether bonds cleavage, and formation of noncyclic sulfur-containing structures. Similar behavior of lignin was observed during kraft pulping with sodium sulfide at 170°C.[14,15] In addition, the corresponding vulcanizates were characterized by FTIR spectroscopy. Figure 9 gives the spectrum of the vulcanized rubber compounded with 20 phr of lignin. It shows, besides the typical rubber vibrations described by Suito and Arakawa,[16] lignin absorption bands that were diminished after ethanol–water extraction. Moreover, the absorption bands corresponding to sulfides in the range 705–570 cm^{-1} vanished.

The revealed differences in the structure of the original lignin and that of the lignin isolated from the

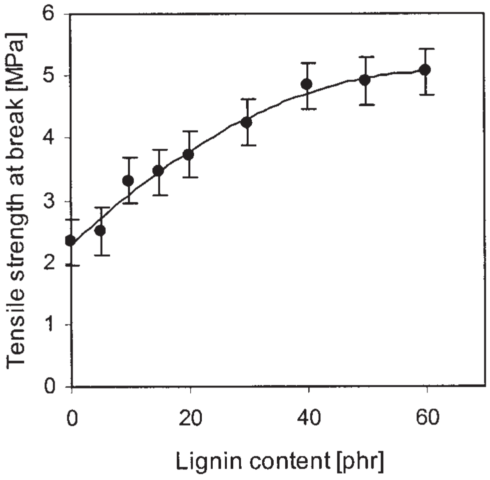

Figure 5 Effect of lignin content on tensile strength at break of vulcanizates.

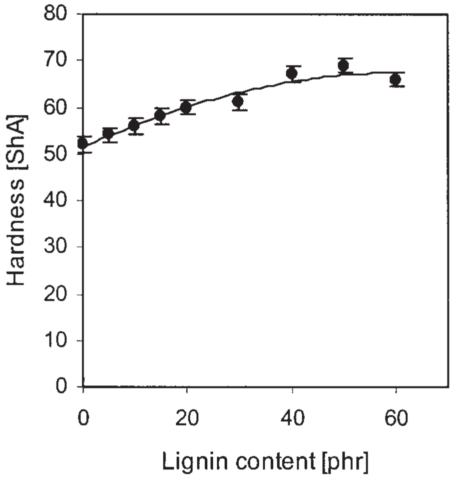

Figure 7 Effect of lignin content on hardness of vulcanizates.

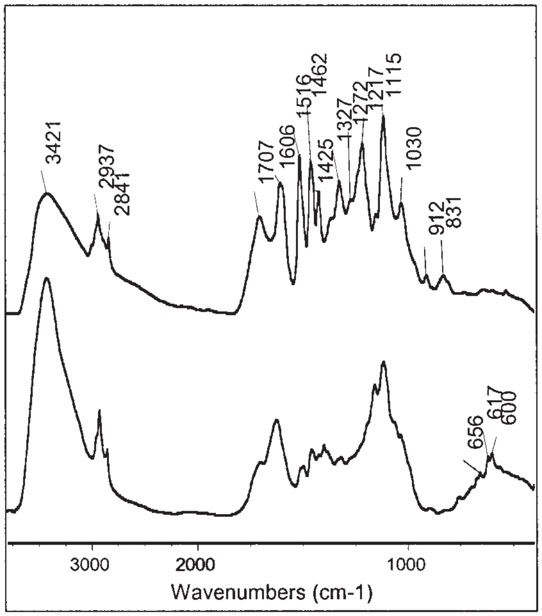

Figure 8 FTIR spectra of lignin preparations: upper spectrum, original lignin; lower spectrum, lignin isolated from SBR vulcanizate compounded with 20 phr lignin.

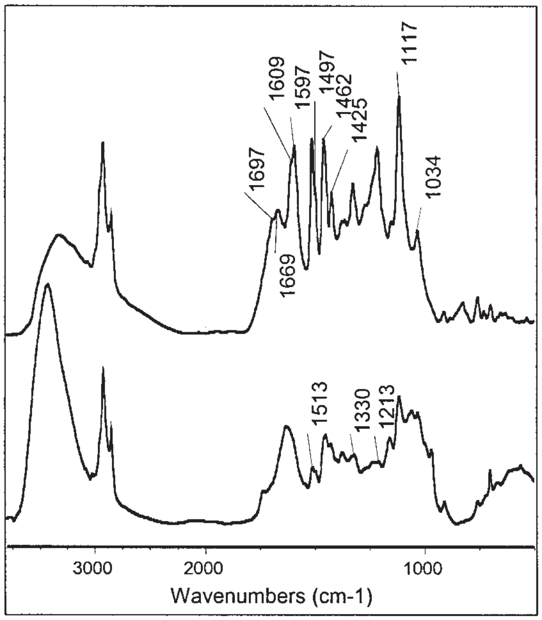

Figure 10 FTIR spectra of SBR vulcanizate compounded with 50 phr lignin: upper spectrum, lignin extract; lower spectrum, vulcanizate after lignin extraction.

rubber blend indicate its interaction with the sulfur system during the vulcanization process. Similarly, as in kraft pulping,[17] lignin structures containing sulfur can be characterized as intermediates, which later probably release sulfur, available for crosslink formation in rubber matrix. FTIR analysis (Fig. 10) of the fraction isolated from the vulcanizate containing 50 phr lignin showed that the extent of structural modification of lignin with sulfur system was negligible. Moreover, several absorption bands at 2920–2852 cm^{-1} (aliphatic C–H stretching) as well as at 1606 and 1496 cm^{-1} (–C=C–aromatic vibration) corresponding to SBR are present in the spectrum of the isolated lignin. The spectrum of the vulcanizate residue after extraction (Fig. 10) showed, besides the typical rubber vibrations, absorption bands attributed to lignin. These results indicate an interaction between lignin and SBR during the vulcanization process. According to Flory,[18] when rubber and carbon black are vulcanized with sulfur, in addition to the crosslinking reaction in the rubber phase, a chemical reaction between the rubber and filler may occur as well as the formation of some modified polymer layers near the boundary surfaces.

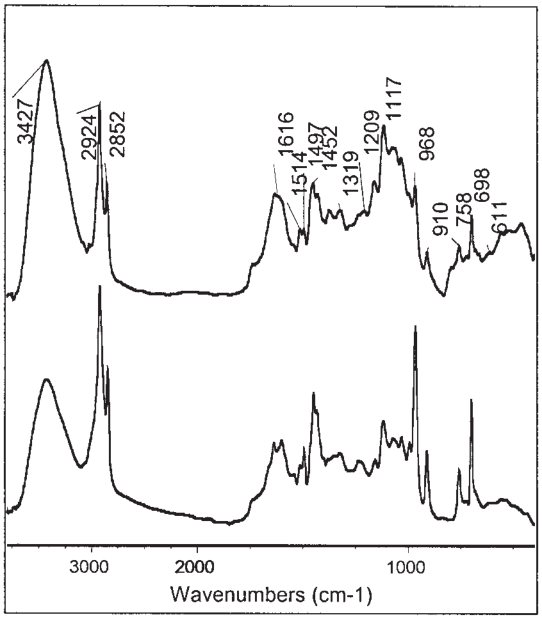

Figure 9 FTIR spectra of SBR vulcanizate compounded with 20 phr lignin: upper spectrum, vulcanizate; lower spectrum, vulcanizate after lignin extraction.

CONCLUSION

Novel SBR composites filled with sulfur-free lignin under sulfur vulcanization were prepared. The obtained results show that lignin biopolymer influences vulcanizing behavior of SBR blends. The addition of lignin in amounts from 20 to 50 phr into SBR rubber blends brings about a significant improvement of physicomechanical properties of the prepared vulcanizates, i.e., stress at 100% elongation, tensile strength at break, and elongation at break. The lignin activity in the vulcanization process was confirmed by measurement of cure characteristics, such as scorch time, optimum cure time, and cure rate index. The determined coefficient of lignin activity of the prepared rubber compounds clearly indicates that the used lignin reinforces rubber blends. The chemical interaction between lignin and the vulcanization system was confirmed by FTIR spectroscopy at loading up to 20 phr lignin. In the case of a higher lignin amount (50 phr) in the vulcanizate, some interfacial interaction between lignin and SBR may occur. The obtained results indicate a great potential for the use of sulfur-free lignin as a component of polymer–elastomer systems. However, further investigation of the functional properties of these composites is necessary for end-use application.

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References

1. Glasser, W. G. Forest Prod J, 1983, 31, 24.
2. Saraf, V. P.; Glasser, W.G. J Appl Polym Sci 1984, 29, 1831.
3. Košíková, B.; Demianová, V.; Kacuráková, M. J Appl Polym Sci 1993, 47, 1065.
4. Alexy, P.; Košíková, B.; Podstránska, G. Polymer 2000, 41, 4901.
5. Košíková, B.; Revajová, A.; Demianová, V. Eur Polym J Mater 1995, 31, 953.
6. Košíková, B.; Mlynár, J.; Joniak, D.; Konigstein, J.; Micko, M. Cellul Chem Technol 1990, 24, 85.
7. Mizumachi, H.; Tsukii, M. Holzforschung 1980, 34, 122.
8. Košíková, B.; Brežný, R.; Ginter, E. Cellul Chem Technol 1984, 18, 405.
9. Košíková, B.; Miklešová, K.; Demianová, V. Eur Polym J Mater 1993, 29, 1495.
10. Falkehag, S. I. J Appl Polym Symp 1975, 28, 247.
11. Kumaran, M. G.; De Sadhan, K. J Appl Polym Sci 1978, 22, 1885.
12. Košíková, B.; Mlynár, J. J Wood Chem Technol 1982, 12, 243.
13. Wolff, S. Kautsch Gummi Kunstst 1970, 23, 7.
14. Sarkanen, K. V.; Chirkin, G.; Hrutfiord, B. F. Tappi J 1963, 46, 375.
15. Field, L.; Drummond, P. E.; Jones, E. A. Tappi J 1958, 41, 727.
16. Suito, E.; Arakawa, M. Rubber Chem Technol 1965, 38, 279.
17. Enkvist, T. Svensk Papperstidn 1957, 17, 616.
18. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: Ithaca, NY, 1953; Chapter 2.