Devulcanization of Carbon Black Filled Natural Rubber Using Supercritical Carbon Dioxide

Masaaki Kojima,[1]* Masatoshi Tosaka,[1] Yuko Ikeda,[2] Shinzo Kohjiya[1]

[1]*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*
[2]*Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Sakyo, Kyoto 606-8585, Japan*

ABSTRACT: Natural rubber (NR) vulcanizates filled with various contents of carbon black were devulcanized in supercritical CO_2 in the presence of diphenyl disulfide as a devulcanizing reagent. The devulcanized rubbers were separated to sol and gel components using chloroform. Regardless of the carbon black content in the NR vulcanizates, sol fractions of 20–40% were obtained and the swelling ratios of the gel components were higher than the original vulcanizates. Dynamic mechanical properties of the devulcanized rubbers were also investigated. Devulcanized rubbers showed a slightly lower G' values and slightly higher tan δ values than the initial compounds and much lower G' values and much higher tan δ values than the vulcanizates. These results indicate that the presence of carbon black in NR vulcanizates does not disturb the devulcanization. A NR-based truck tire vulcanizate was also devulcanized. The physical properties of recycled rubber made from virgin rubber and various contents of the devulcanized tire rubber were measured. The decrease in tensile strength was only around 10% at up to 40 phr of the devulcanized tire rubber content. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 137–143, 2005

INTRODUCTION

The problem of used rubber products must be confronted by the rubber industry.[1] Various ways to deal with used rubber products have been developed.[2–7] Reclaiming is, at the moment, one reasonable methods for handling the problem. The general reclaiming procedure consists mainly of two processes.[8–11] Used rubber products are first chopped into pieces and ground into fine particles. In the second procedure, the particles are subjected to a devulcanization process, which includes scission of the existing sulfur crosslinks (devulcanization) and/or of the polymer main chains (depolymerization) in the used rubber (vulcanizate), and permits their reuse as an additive for the manufacture of new rubber compounds. The reclaimed rubber has been widely used in tire compounding for lowering cost, improving processibility, and improving fatigue strength. However, radial tires do not use reclaimed rubber because they require higher abrasion resistance that cannot be attained by mixing reclaimed rubber. Better processes for the production of higher quality reclaimed rubber will be needed in order to use it for the radial tires. In order to improve the quality of reclaimed rubber, crosslinks in vulcanizate should be severed selectively during a devulcanization process and no low-molecular-weight compound such as swelling solvent should remain in the reclaimed rubber after the devulcanization process. Such selective devulcanization processes have been studied in order to improve the productivity and quality of reclaimed rubber; chemical,[12,13] chemomechanical,[14–18] mechanical,[19] thermomechanical,[20] microwave[21] and ultrasound[22,23] methods have been reported. However, no devulcanization process with compatibility between productivity and quality has been established.

The authors developed a devulcanization process that utilizes supercritical CO_2 (scCO_2) as a devulcanization reaction medium in the presence of a devulcanizing reagent. Supercritical fluids (SCFs) show unique physicochemical properties: they are of low viscosity, high diffusivity, and high thermal conductivity.[24–26] Impregnation of a low-molecular-weight substance into a 3-dimensional network polymer system is expected to be enhanced by using SCFs as a reaction medium.[27–31] Among several SCFs, CO_2 is the most advantageous for the current purpose because it is chemically inactive, nontoxic, nonflammable, and inexpensive. Residual CO_2 in the polymer matrix is easily and rapidly removed by releasing pressure. Furthermore, CO_2 has an easily accessible critical point (the critical temperature and the critical pressure are 31.1°C and 7.38 MPa, respectively). Therefore,

Ingredient	NR-0	NR-20	NR-40	NR-60
NR	100	100	100	100
HAF carbon black		20	40	60
Zinc oxide	2	2	2	2
Stearic acid	2	2	2	2
DG[b]	0.3	0.3	0.3	0.3
CBS[c]	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5

[a] The values are in parts per hundred rubber in weight (phr).
[b] Diphenyl guanidine.
[c] N-Cyclohexyl-2-benzothiazole sulfenamide.

$scCO_2$ is also expected to be applicable as a devulcanization reaction medium. We already reported the devulcanization process using $scCO_2$ for unfilled polyisoprene rubber vulcanizates[32] and unfilled natural rubber (NR) vulcanizates.[33] These unfilled vulcanizates were ascertained to be effectively devulcanized by the devulcanization process. The optimum condition for the devulcanization of the unfilled rubber was determined in previous studies. On the other hand, most practical rubber products, such as tire rubber, contain carbon black as a reinforcing filler.

Carbon black has a great effect on the chemical and physical properties of a rubber compound. The presence of carbon black in a rubber compound causes a significant increase in the cure rate by the chemical groups on the surface.[34] Carbon black tends to reduce the swelling of a vulcanizate in a manner that is proportional to the filler content, while the crosslink density in the rubber compound remains unchanged.[35,36] Diffusivity of gases for NR vulcanizate depends on carbon black content as well; the higher the fraction of carbon black the less diffusivity.[37] Therefore, carbon black has the possibility of affecting devulcanization using $scCO_2$.

In this paper, the effect of carbon black on devulcanization was investigated for the NR vulcanizate. Devulcanization of a NR-based truck tire vulcanizate as a typical example of industrial products was also investigated as a further step toward the practical application of this technique.

EXPERIMENTAL

Materials

RSS#3 was used as NR. Butadiene rubber, BR01, was provided from JSR Co. Sulfur including oil of 5% by weight was provided from Hosoi Chemical Co. and used for curing. N339 carbon black was purchased from Mithubishi Chemical Co. Aromatic oil, X140, was purchased from Japan Energy Co. Antioxidant, Santflex 6PPD, was purchased from Flexsys Co. Diphenyl

guanidine was purchased form Ouchishinko Chemical Industrial Co. N-Cyclohexyl benzothiazyl sulfenamide was purchased from Sumitomo Chemical Co. Diphenyl disulfide (mp 58–60°C) was purchased from Nacalai Tesque, Inc., and was used as a devulcanizing reagent. Liquid carbon dioxide was purchased from Kyoto Teisan Co.

Preparation of filled NR vulcanizates

Model vulcanizates of filled NR

Formulations for model compounds of filled NR with various contents of HAF (high abrasion furnace) carbon black are shown in Table I. Each compound was prepared by mixing in a Banbury mixer, according to a two-stage mixing procedure. The curing properties of the compounds are shown in Table II. Each compound was cured at 141°C for 30 min to be a vulcanizate sheet. "Compound" means an uncured compound in this paper.

NR-based truck tire vulcanizate and recycled rubber made from virgin rubber and devulcanized rubber

A NR-based truck tire vulcanizate was prepared according to an industrially practiced formulation shown as the compound "ini-TT" in Table III. Formulations for recycled rubber made from virgin rubber and devulcanized rubber are also shown in Table III. (The net content of ingredients in the blended new compounds except the antioxidant and curatives was calculated so as to be equal in all compounds.) Each compound was mixed using an 8-inch two-roll mill. The compound was cured at 141°C for 30 min to be a vulcanizate sheet.

Devulcanization reactions

A vulcanizate sample piece of 2.0 g was cut from the vulcanizate sheet of 2.5-mm thickness. The vulcanizate sample piece(s) of 2.0 g (50 g) and diphenyl disulfide of 0.22 g (5.5 g) as a devulcanizing reagent were loaded in an autoclave with 52-mL (500-mL) volume. (The values in parentheses are for the case of devulcanization of the NR-based truck tire vulcanizate.) After the autoclave lid was closed, a certain

	t_{90} (min)	M_L (dNm)	M_H (dNm)
NR-0	19	0.6	7.9
NR-20	10	1.0	11.5
NR-40	9	2.0	16.7
NR-60	7	3.2	21.1

[a] Measured at 141°C.

TABLE III
TABLE III
Formulations of a NR-Based Truck Tire Compound and Recycled Rubber Compounds Made from Virgin Rubber and Devulcanized Rubber[a]

Ingredient	ini-TT	TT-re20	TT-re40	TT-re60
NR	93	83.7	74.4	65.1
BR	7	6.3	5.6	4.9
DR[b]		20	40	60
HAF carbon black	70	63	56	49
Aromatic oil	20	18	16	14
Zinc oxide	2	2	2	2
Stearic acid	2	2	2	2
Antioxidant[c]	2	2	2	2
DG[d]	0.3	0.3	0.3	0.3
CBS[e]	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5

[a] The values are in parts per hundred rubber in weight (phr).
[b] DR, devulcanized rubber.
[c] Santflex 6PPD.
[d] Diphenyl guanidine.
[e] *N*-Cyclohexyl-2-benzothiazole sulfenamide.

amount of CO$_2$ was purged into the autoclave. Then, the autoclave was heated to 180°C and maintained at that temperature under a pressure of 10 MPa. After 60 min of reaction, the autoclave was cooled to room temperature and depressurized. The product, namely devulcanized rubber, was taken up from the autoclave.

Analyses

Curing properties

Curing properties of the model compounds were measured by Monsanto Rheometer MDR200. M_L and M_H are minimum torque and maximum torque attained during the test, respectively. The M_L is generally a measure of the rubber's resistance to flow during processing, while the M_H is related to the compound's final stiffness. t_{90} (minutes to 90% of maximum torque) indicates the cure time required to almost complete the vulcanization.

Acetone and chloroform extractions

Small pieces of each of the model compounds, the vulcanizates, and the devulcanized rubbers were subjected to acetone and/or chloroform extraction. Residual curatives and/or the devulcanizing reagent that have not reacted with the polymer chains are found in the acetone extract; polyisoprene is insoluble in acetone. For the acetone extraction, samples of ca. 50 mg were subjected to Soxhlet extraction using acetone as solvent for 8 h and the residues were dried *in vacuo.* For the chloroform extraction, the residues after acetone extraction, which were acetone-insoluble prod-

ucts, were placed in chloroform (20 ml, changed to fresh solvent every day) at room temperature for 3 days. The chloroform solutions containing insoluble portions were filtered to separate sol and gel components. Both the sol and the gel components were dried again *in vacuo* at room temperature to constant weight.

Sulfur content analyses

Sulfur contents were measured with a sulfur analyzer from LECO (model SC432) that detects the amount of SO$_2$ generated by complete combustion of the sample.

Swelling studies

The equilibrium swelling experiments were carried out by immersing the samples in toluene for 3 days at 25°C. The swelling degree is expressed in terms of the ratio of the swollen volume to the original volume.

Dynamic mechanical properties

Dynamic mechanical analyses were performed using a Soliquid meter (Model No. MR-500, Rheology Co.) under a torsion strain mode between parallel plates with sinusoidal wave. The experiments were carried out using a corn plate of 2.00-cm diameter at a frequency of 1.0 Hz, a strain of 0.1 deg, and a constant load of 1500 *g* at 23°C. The specimens were cylindrical with ca. 2.5-mm thickness and 2.00-cm diameter.

Tensile measurements

Tensile tests were performed with a Tensile tester (Model No. TS-3030, Ueshima Seisakusho Co.) in accordance with JIS K6301 at a crosshead speed of 500 mm/min. The average value of four measurements was reported as the result of the tensile test.

Hardness measurements

Hardness tests were performed with a hardness tester of type JA, according to JIS K6301.

RESULTS AND DISCUSSION

The effect of carbon black on devulcanization

Model vulcanizates of filled NR with various contents of HAF carbon black were devulcanized in order to investigate the effect of carbon black on devulcanization. The devulcanized rubbers were characterized and their physical properties examined.
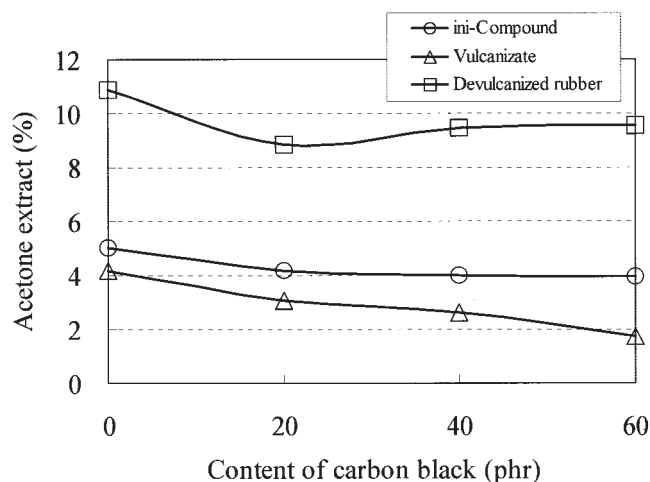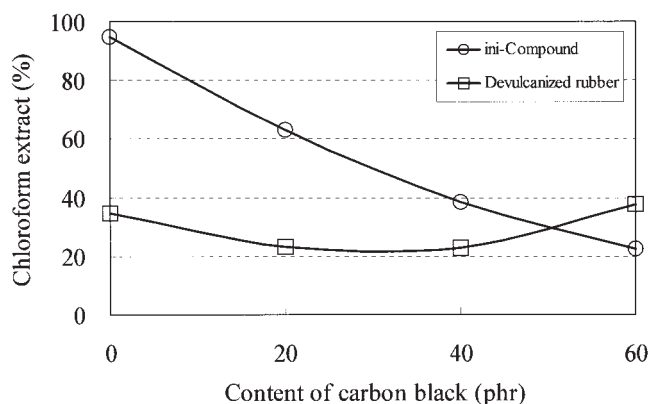
Figure 1 The effect of carbon black content on acetone extracts of model compounds of filled NR, the vulcanizates, and the devulcanized rubber.

Characterizations of the devulcanized model vulcanizates

Acetone and chloroform extractions

The amounts of acetone from the model compounds, the vulcanizates, and the devulcanized rubbers are compared in Figure 1. The amounts of acetone extracts from the vulcanizates tended to decrease with the increase in carbon black content, because the higher content of carbon black leads to the smaller net amount of extractable curatives in the samples according to the formulations. On the other hand, the amounts of acetone extracts from the devulcanized rubbers with carbon black content of over 20 phr remained roughly constant. The difference in the amount of acetone extracts (between the vulcanizate and the devulcanized rubber) is a measure of the amount of the devulcanizing reagent incorporated into the sample during devulcanization. The difference increased slightly with the increase in carbon black content. According to the results in Figure 1, the amount of devulcanizing reagent that was transferred and incorporated into the sample during devulcanization was estimated to be 53–71% of that added in the autoclave before devulcanization. This result indicates that carbon black does not block the incorporation of the devulcanizing reagent into the vulcanizate.

The amounts of chloroform extracts from the model compounds and the devulcanized rubbers are compared in Figure 2. The amounts of chloroform extracts from the initial compounds decreased greatly with the increase in carbon black content. This result is reasonable although the initial compounds are not cured, because the formation of bound rubber due to the carbon filler should reduce the extractable polymer. On the other hand, the amounts of chloroform extracts from the devulcanized rubbers decreased slightly with

Figure 2 The effect of carbon black content on chloroform extracts of model compounds filled NR and the devulcanized rubber.

the carbon black content up to 40 phr and increased over 40 phr. The amount of chloroform extract that is mostly uncrosslinked polymer is a measure of the progress of devulcanization reaction. Devulcanization apparently proceeded more easily with the increase in carbon black content. This may be due to the increased fraction of the devulcanizing reagent to the polymer because the amount of devulcanizing reagent was kept constant, although the net amount of the polymer in the vulcanizates decreased with the increase in carbon black content.

From the results of the acetone and chloroform extractions mentioned above, it is noted that the presence of carbon black does not disturb devulcanization.

Swelling ratios of the gel components

The swelling ratios of the model vulcanizates and the gel components in the devulcanized rubbers were measured. The results are shown in Table IV. The swelling ratios of the gel components of the devulcanized rubbers were higher than those of the original vulcanizates. The higher swelling ratio indicates a lower crosslink density of the sample.

TABLE IV
Swelling Ratios of the Model Vulcanizates of Filled NR and the Gel Components of Devulcanized Rubber with Various Contents of Carbon Black[a]

Content of carbon black (phr)	Vulcanizates	Gel components of the devulcanized rubbers
0	5.9	15.0
20	4.9	9.4
40	4.2	5.7
60	3.7	4.5

[a] Measured by immersing the samples in toluene for 3 days at 25°C.
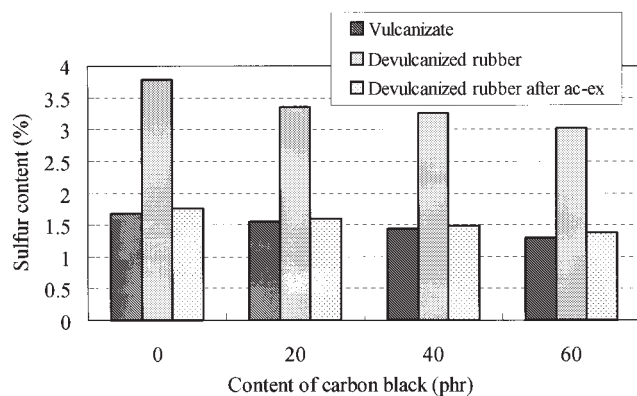
Figure 3 Comparison of sulfur contents in the original vulcanizates, the devulcanized rubbers, and the devulcanized rubbers after acetone extraction with a variety of carbon black contents.

Figure 4 Comparison of G' of the initial model compounds, the vulcanizates, and the devulcanized rubbers with a variety of carbon black contents.
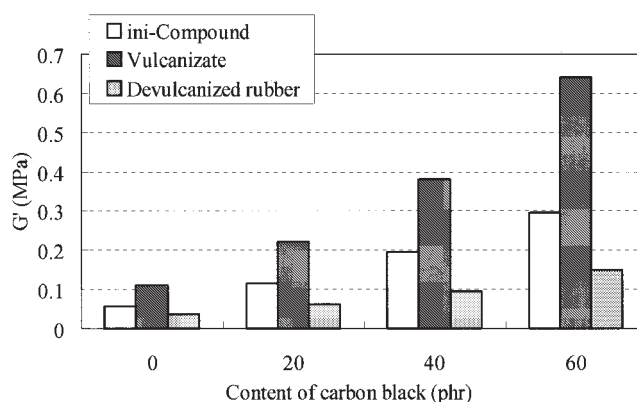
Sulfur contents

Sulfur contents are shown in Figure 3 for the original model vulcanizates, the devulcanized rubber, and the devulcanized rubbers subjected to acetone extraction. The devulcanized rubbers showed much higher sulfur contents than the original vulcanizates. The increase in the sulfur contents during devulcanization is due to the incorporation of the devulcanizing reagent that contains sulfur, as shown in Figure 1. The carbon black content had little effect on the sulfur content. This result also indicates that the presence of carbon black does not block the incorporation of the devulcanizing reagent into a vulcanizate. The amount of devulcanizing reagent transferred and incorporated into the vulcanizates during devulcanization was estimated to be 58–68% of that added in the autoclave before devulcanization. The values calculated here are almost consistent with the values calculated from the acetone extracts and are supposed to be more accurate. Sulfur contents of the devulcanized rubbers after acetone extraction were apparently lower than those of the original devulcanized rubber. The decreased amounts are interpreted to be due to unreacted devulcanizing reagent and/or residual sulfur removed from crosslinks.

Physical properties of the devulcanized model rubbers

Dynamic mechanical properties

Dynamic mechanical properties (G' and tan δ) of the devulcanized rubbers were measured.

The G' of the devulcanized rubbers were a little lower than those of the initial compounds and much lower than those of the vulcanizates, as shown in Figure 4. The reduction of G' indicates that crosslinks

and/or polymer main chains were broken during devulcanization.

Tan δ values of all devulcanized rubbers were almost same and were much higher than those of the original vulcanizates, as shown in Figure 5. It is supposed that scission of crosslinks during devulcanization progressively increases tan δ because the chain segment between crosslinks, and hence the distance they can move on deformation, becomes longer. Tan δ values of the devulcanized rubbers were a little higher than those of the initial compounds, as shown in Figure 5. The increase in the tan δ value indicates that the devulcanized rubbers contain more branched polymer chains than the initial compounds.

The relative processing performance of a compound in the manufacturing process for rubber products is dependent upon its plasticity/elasticity relationship. Devulcanized rubbers with any carbon black content were expected to have good processibility because the devulcanized rubbers had lower G' and higher tan δ values than the initial compounds.
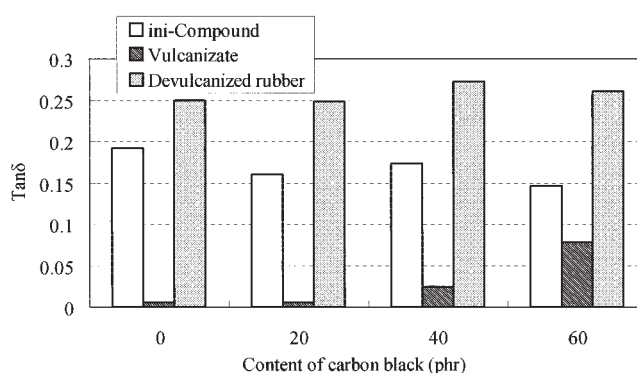
Figure 5 Comparison of tan δ of the initial model compounds, the vulcanizates, and the devulcanized rubbers with a variety of carbon black contents.

TABLE V
Physical Properties of the Devulcanized NR-Based Truck Tire Rubber/Virgin Rubber Blended Vulcanizates

	Hardness[a]	M100[b] (MPa)	T_b^c (MPa)	E_b^d (%)
ini-TT	62	3.9	30.3	460
TT-re20	67	4.0	29.6	460
TT-re40	70	5.0	26.7	380
TT-re60	69	4.8	24.5	400

[a] In accordance with JIS K6301.
[b] Modulus at 100% elongation.
[c] Tensile strength at break.
[d] Elongation at break.

The results of the dynamic mechanical measurements also indicate that the presence of carbon black does not disturb the progress of devulcanization.

Devulcanization of a NR-based truck tire vulcanizate

Devulcanization of a NR-based truck tire vulcanizate as a typical carbon black filled NR product was investigated as the next step toward the practical application devulcanization. In addition to the ingredients in the model vulcanizates of filled NR, butadiene rubber, (BR), aromatic oil, and antioxidant were compounded in the NR-based truck tire vulcanizate. The formulation used here is typical for truck tire tread compounds and is shown as compound ini-TT in Table III. Devulcanization of the truck tire vulcanizate was carried out under the same conditions used in the study on devulcanization of model vulcanizates.

The devulcanized rubber was blended with virgin rubber according to the formulations TT-re20, TT-re40, and TT-re60 in Table III. The compounds were vulcanized again to be recycled rubber. Physical properties of the recycled rubber with various content of the devulcanized rubber were measured.

Physical properties of recycled rubber made from virgin rubber and devulcanized truck tire rubber

Physical properties of the recycled rubber are shown in Table V. No deterioration on the tensile property was observed for TT-re20. The modulus at 100% elongation (M100) of TT-re40 and TT-re60 was considerably higher than that of the original vulcanizate (ini-TT); for TT-re40, M100 increased by 28% compared to the original vulcanizate. The hardness of all recycled rubber samples was also higher than that of the original vulcanizate. Residual sulfur in the devulcanized tire rubber is thought to have worked as a crosslink agent in the recycled compounds.[33,34] The tensile strength at break (T_b) of the recycled rubber decreased slightly with the increase in the devulcanized tire rub-

ber content. This decrease of T_b may have been caused mainly by the low-molecular-weight component in the devulcanized rubber. The relatively poor T_b of the recycled rubber is strongly supposed to be due to the polymer structural changes that occurred during the devulcanization process. However, the decrease in T_b was only around 10% up to 40 phr of the devulcanized tire rubber content. Adhikari *et al.* have devulcanized NR vulcanizate by mechanical milling in the presence of a reclaiming reagent and prepared recycled rubber with it.[18] In their report, at a devulcanized NR content of 40 phr, the tensile strength decreased to around 80%. In our case, around 90% of the original tensile strength was retained, as shown in Table V. Because our devulcanization process has no intensive mechanical shearing, scission of polymer main chain may have been reduced.

Devulcanized rubber can serve for a practical application with the combination of virgin rubber.

CONCLUSIONS

Carbon black filled NR vulcanizate was devulcanized sufficiently by the devulcanization method using scCO$_2$. This devulcanization process using scCO$_2$ was not disturbed by the presence of carbon black. The devulcanized rubber with various carbon black contents was expected to have good processibility. A NR-based truck tire vulcanizate was also devulcanized. The devulcanized tire rubber can serve a practical use with the combination of virgin rubber.

References

1. Liu, H. S.; Mead, J. L.; Stacer, R. G. Rubber Chem Technol 2000, 73, 551.
2. Stafford, W. E.; Wright, R. A. Rubber Chem Technol 1958, 31, 599.
3. Le Beau, D. S. Rubber Chem Technol 1967, 40, 217.
4. Beckman, J. A.; Crane, G.; Kay, E. L.; Laman, J. R. Rubber Chem Technol 1974, 47, 597.
5. Schnecko, H. Kautsch Gummi Kunstst 1994, 47, 885.
6. Adhikari, B.; De, D.; Maiti, S. Prog Polym Sci 2000, 25, 909.
7. Myhre M.; MacKillop, D. A. Rubber Chem Technol 2002, 75, 429.
8. Owen, E. W. Rubber Chem Technol 1944, 17, 544.
9. Le Beau, D. S. Rubber Chem Technol 1948, 21, 895.
10. Cook, W. C. Rubber Chem Technol 1948, 21, 166.
11. Amberlang, J. C.; Smith, G. E. P.,; Jr., Rubber Chem Technol 1955, 28, 322.
12. Yamashita, S.; Kawabata, N.; Sagan, S.; Hayashi, K. J. Appl Polym Sci 1977, 21, 2201.
13. Nicholas, P. P. Rubber Chem Technol 1982, 55, 1499.
14. Menadue, F. B. Rubber Age, 1945, 56, 511.

15. Cunneen, J. L. Rubber Chem Technol 1968, 41, 182.
16. Okamoto, H.; Inagaki, S.; Onouchi, Y.; Furukawa, J. Int Polym Sci Technol 1980, 7, 59.
17. Verbruggen, M. A. L.; van der Does L.; Noordermeer, J. W. M. Rubber Chem Technol 1999, 72, 731.
18. De, D.; Maiti, S., Adhikari, B. J. Appl Polym Sci 1999, 73, 2951.
19. Phadke, A. A.; Bhattacharya, A. K.; Chakraborty, S. K.; De, S. K. Rubber Chem Technol 1983, 56, 726.
20. Mouri, M.; Sato, N.; Okamoto, H.; Matushita, M.; Honda, H.; Nakashima, K.; Takeuchi K.; Suzuki, Y.; Owaki, M. Nippon Gomu Kyokaisi 1999, 72, 43.
21. Fix, S. R. Elastomerics 1980, 112, 92.
22. Isayev, A. I.; Chen J. Tukachinsky, A. Rubber Chem Technol 1995, 68, 267.
23. Hong, C. K.; Isayev, A. I. J. Appl Polym Sci 2001, 79, 2340.
24. Chang, S. H.; Park, S. C.; Shim, J. J. J Supercrit Fluids 1998, 13, 113.
25. Kajimoto, O.; Tucker S. C.; Peters, C. J.; Gauter, K.; Brennecke, J. F.; Chauteauneuf, J. E.; Baiker, A.; Jessop, P. G.; Ikariya, T.; Noyori, R.; Darr, J. A.; Poliakoff, M.; Kendall, J. L.; Canelas, D. A.; Young, J. L.; DeSimone, J. M.; Kirby, C. F.; McHugh, M. A.; Savage P. E.; Mesiano, A. J.; Beckman, E. J.; Russell, A. J. Chem Rev 1999, 99, 353.
26. Perrut, M. Ind. Eng Chem Res 2000, 39, 4531.
27. Berens, A. R.; Huvard, G. S.; Korsmeyer, R. W.; Kunig, F. W. J Appl Polym Sci 46, 1992, 231.
28. Watkins, J. J.; MaCarthy, T. J. Macromolecules 1994, 27, 4845.
29. Kazarian, S. G.; Brantley, N. H.; West, B. L.; Vincent, M. F.; Eckert, C. A. Appl Spectrosc 1997, 51, 491.
30. von Schnitzler, J.; Eggers, R. J Supercritical Fluids 1999, 16, 81.
31. Wang, Y.; Yang, C.; Tomasko, D. Ind Eng Chem Res 2002, 41, 1780.
32. Kojima, M.; Ogawa, K.; Mizoshima, H.; Ikeda, Y.; Tosaka, M.; Kohjiya, S. Rubber Chem Technol 2003, 76, 957.
33. Kojima, M.; Tosaka, M.; Ikeda, Y. Green Chem 2004, 6, 84.
34. Wampler, W. A.; Gerspacher, M.; Yang, H. H. Rubber World 1994, 210, 1.
35. Lorenz, O.; Parks, C. R. J Polym Sci 1961, 50, 299.
36. Kraus, G. J Appl Polym Sci 1963, 7, 861.
37. Dawson, T. R.; Porritt, T. R. Rubber Physical and Chemical Properties; Research Association of British Rubber Manufacturers: Croydon, UK, 1935; p 466.