

## Modified carbon black as reinforcing filler for SBR

Arup Kumar Ghosh, Sukumar Maiti & Basudam Adhikari\*  
Materials Science Centre, Indian Institute of Technology, Kharagpur 721 302, India

Received 18 July 1996; accepted 16 December 1996

Carbon black HAF (N330) was treated with an unsaturated hydroxy organic fatty acid in presence or absence of dicumyl peroxide for the attachment onto carbon black as a flexible bridge between filler surface and elastomer chain to improve some of its reinforcement behaviours in SBR vulcanizates. The treated black was characterized and evaluated for its processing behaviour and the level of reinforcement in SBR. It was found that the surface modification with the organic fatty acid resulted in a considerable improvement of processing as well as vulcanizate properties, such as, tensile strength, abrasion resistance and flex crack growth resistance.

Modification of carbon black filler and subsequent evaluation of its reinforcing action in different synthetic and natural rubbers have long been a subject of study of many researchers. Grafting of selected oligomers and polymers onto the black surface, surface oxidation, use of different promoters or coupling agents, and reaction of various reactive compounds with carbon black are worth noticing among the methods developed till date. Donnet and collaborators<sup>1-7</sup> grafted polymers onto carbon black with an objective to make it more efficient as a filler. But the polymer grafted-carbon black could not bring a marked improvement in the reinforcing behaviour in most of the cases. Dannenberg and coworkers<sup>8,9</sup> proposed the concept of deactivation of the surface of carbon black when grafted with polymers. In some recent studies, Vidal and associates<sup>10</sup> grafted alkyl chains to carbon black and reported a weak filler polymer interaction due to the grafting. Use of silane compounds for grafting also resulted in a decrease of reinforcing effect of carbon black<sup>11</sup>.

Many chemical promoters were developed during the last fifty years for use as coupling agents between the carbon black surface and elastomers and for higher reinforcement in products based on natural, styrene-butadiene, butyl and nitrile rubbers. In most cases only little improvement in some properties at the cost of some others was observed. Rivin and Dannenberg<sup>12</sup> attached such organic functional groups as  $-\text{NH}_2$ ,  $-\text{NHCH}_3$ ,  $-\text{N}(\text{CH}_3)_2$ ,

$-\text{NHCH}_2\text{CH}=\text{CH}_2$ , and  $-\text{OOH}$  to the carbon black surface as a means of chemical modification. Such modifications resulted relatively small changes in the bound rubber reactivity, and in moduli and tensile properties in vulcanizates of SBR, *cis*-polybutadiene and butyl rubber.

However, some patents were published for use of modified carbon black in SBR vulcanizates. Furukawa and coworkers<sup>13</sup> obtained enhanced reinforcing properties in SBR after increasing the active hydrogen content of carbon black by modifying with diethylene glycol, ethanolamine, hexamethylene diamine, 1,2-dimercaptopropyl alcohol or phenylisocyanate. Some improvements in properties were obtained by fatty acid modifications of carbon black in two patents<sup>14,15</sup>. Gajewski and Prot<sup>16</sup> have shown increased crosslink density and improved strength properties in SBR using carbon black modified by treatment with  $\text{S}_8$ ,  $\text{CS}_2$ ,  $\text{SO}_2$  and  $\text{H}_2\text{S}$ . But the cause for improvement of the vulcanizate properties by such modifications was not understood properly. Recently, the present authors have reported some improvements in the reinforcing behaviour of some modified carbon blacks in SBR<sup>17,18</sup>. The major objectives of the studies reported in the present communication have been to achieve better processing behaviour and improved vulcanizate properties with an organic fatty acid modified carbon black.

### Experimental Procedure

*Materials*—SBR 1502 (Synthetics and Chemicals Ltd), carbon black N 330 (Philips Carbon Black Ltd), dicumyl peroxide (DCP) (BDH, England),

\*For correspondence

CBS (ICI), unsaturated hydroxy organic fatty acid (proprietary agent), zinc oxide (BDH). Other reagents/compounds such as acetone and toluene all AR grade chemicals, and commercial grades of stearic acid, sulphur and spindle oil were used as received.

A solution of the organic fatty acid and the peroxide in acetone were mixed with carbon black, air dried at room temperature for 24 h and then heated at 140-150°C.

**Carbon black characterization**—Fatty acid treated carbon black samples were extracted by acetone in a soxhlet for 30-40 h. The extracted carbon blacks were dried to constant weight and characterized for surface area (by ASTM D1510 procedure) and structure (by ASTM D2414 method). The pH of the carbon black samples was also measured with an aqueous slurry containing 5 g black in 25 mL deaerated distilled water and a few drops of acetone by using a pH meter, model EC-5652 ECL, India. Measurement time was allowed upto constant pH.

**Rubber compounding and vulcanization characteristics**—Compounding of SBR was done in a two-roll mixing mill at a friction ratio 1.2. Mixing temperature of the compound was recorded with a thermocouple at a constant time interval. To estimate the bound rubber content the rubber compounds were kept at room temperature for seven days for conditioning. Approx. 0.5 g of such sample was immersed in 250 mL of toluene in a stainless steel wire cage (320 mesh). The solvent was renewed every 24 h and after 5 days the residue was taken out of the solvent and vacuum dried to constant weight. The bound rubber content was expressed as the weight per cent of the polymer left as carbon gel<sup>19</sup>.

The cure characteristics of the compounds were analyzed using a Monsanto Rheometer (R-100) at 150°C as per ASTM D2084-81.

**Testing**—Samples for physical testing were cured in an electrically heated hydraulic press (Carver, model 2518) at 150°C and 8 ton pressure (ram dia 2.562") for the respective optimum cure times. Tensile properties were measured by a tensile testing machine (KM1, model 1.3 D) following ASTM D412-51T method. Flex crack growth resistance was tested with a De Mattia Flex Tester (Prolific Engineer) as per ASTM D813-59. Abrasion loss was evaluated by a Du Pont abrasion tester (Prolific Engineer). Heat build up test was carried

Table 1—Formulation of carbon black (CB) for modification

CB designation	Carbon black, g	Acid, g	DCP, g
CB I <sup>a</sup>	100	—	—
CB II <sup>b</sup>	100	—	—
CB III <sup>a</sup>	100	10	—
CB IV <sup>b</sup>	100	10	—
CB V <sup>b</sup>	100	10	1.0
<sup>a</sup> No heat treatment.			
<sup>b</sup> Heat treated under mild operation			

out with the cylindrical samples by Goodrich Flexometer as per ASTM D623-78 method. For the determination of swelling value ( $Q$ ), the cured samples were immersed in 200 mL toluene to equilibrium swelling. The samples were taken out of the solvent and weighed immediately. The swelling value ( $Q$ ) of cured samples was calculated by the following equation:

$$Q = \frac{\text{Swollen weight} - \text{dried weight}}{(\text{original weight of cured sample} \times 100) / \text{formula weight}}$$

where, formula weight is the total weight of rubber plus compounding ingredients based on 100 parts of rubber<sup>20</sup>.

## Results and Discussion

**Carbon black modification**—Rubber grade carbon black has got reactive organic functional groups and free radicals on its surface and it is chemically active<sup>21,22</sup>. Such carbon black was modified with the unsaturated organic fatty acid which is likely to be chemically linked to the carbon black through free radicals or through functional groups. In the actual modification, carbon black was mixed with the unsaturated fatty acid followed by heating in presence or absence of DCP. Compositions of carbon black samples are shown in Table 1. CB I and CB II were used as control where CB I was not heated to compare the effect of heating on modification of others (CB II, CB IV, CB V). CB IV was modified with the fatty acid only whereas CB V was modified with the fatty acid along with DCP to facilitate grafting reaction. In CB III, carbon black was soaked with the acid to see the improvement in reinforcement characteristics.

**Characterization of modified carbon black**—Table 2 describes the characterization of modified carbon black along with the control. The acetone extracted carbon blacks (unmodified and modified) were characterized by gravimetric

analysis, estimation of the surface area by  $I_2$ -adsorption, determination of the structure by dibutylphthalate adsorption (DBPA) and measurement of pH of the aqueous slurry (Table 2). Gravimetric analysis of the soxhlet extracted samples shows the percentage attachment of the organic fatty acid with carbon black on modification. There is 18.02% attachment of acid with the carbon black (CB IV) by simple heating at 140-150°C whereas the bound acid content increases to 25.36% (CB V) on heating in presence of DCP. So, this result shows a positive contribution of peroxide in forming some type of covalent linkages between the fatty acid and the carbon black. Both  $I_2$  and DBP adsorption values get measurably decreased due to the modification outlined. Reduction in surface area and structure of the carbon black is merely due to the action of the modifying agents (acid, peroxide) which form strong linkages with carbon black. pH of the aqueous slurry of the modified carbon black is measurably lower than that produced by the parent carbon black. This is due to the increase in acid content of carbon black after modification with an acidic compound.

**Rubber compounding**—The modified carbon blacks were evaluated in SBR vulcanizates for their roles as processing aid and reinforcing agents. Table 3 shows the formulations of the rubber compounds. Formulations 7 and 8 contain the modified carbon

Table 2—Characteristics of modified carbon black

CB designation	Bound org. acid on CB, %	$I_2$ surface area, $m^2/g$	DBPA value, mL/100 g	pH of aq. slurry
CB I	-	80.2	102.1	7.2
CB IV	18.02	75.3	96.6	5.6
CB V	25.36	74.3	94.8	5.2

Table 3—Mix formulation of rubber compounds

Ingredients, phr	Formulation number							
	1	2	3	4	5	6	7	8
CB I	45	—	—	41	41	—	—	—
CB II	—	45	41	—	—	—	—	—
CB III	—	—	—	—	—	45	—	—
CB IV	—	—	—	—	—	—	45	—
CB V	—	—	—	—	—	—	—	45
Organic acid (as processing aid)	—	—	—	—	4	—	—	—
Spindle oil (as processing aid)	—	—	4	4	—	—	—	—

Base formulation (phr): SBR 1502: 100, ZnO: 5, Stearic acid: 2, CBS: 1, Sulphur: 1.75.

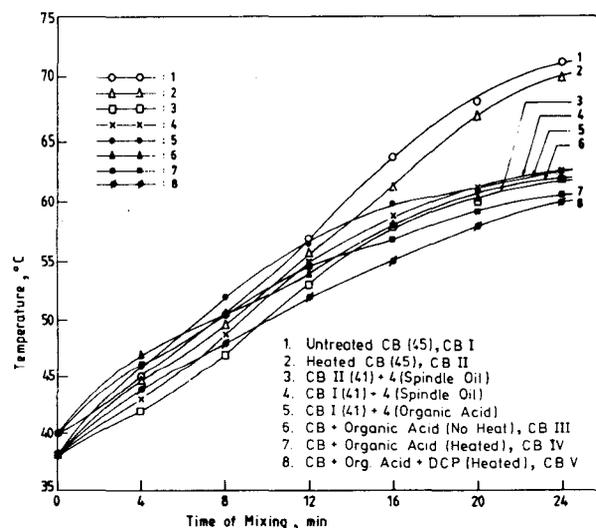


Fig. 1—Plot of temperature vs time of mixing of different black filled formulations

blacks without process oil, whereas formulations 1 to 4 were taken as control containing unmodified carbon blacks. Formulations 1 and 2 do not contain any process oil. Formulation 5 was made to examine the processing aid function of the fatty acid if any. Formulation 6 was made to test the effect of the organic acid present in the physical mixture with the carbon black on the reinforcing properties of the vulcanizate.

**Processing behaviour**—To compare the processing behaviour of modified carbon black the temperature rise of the carbon black rubber mix was monitored during milling. Viscosity average molecular weight of the compounded rubber was measured to evaluate the extent of chain scission on milling and the variance ( $\sigma^2$ ) for test results using 4 to 5 specimens in each case for their tensile strength and modulus values was also estimated to assess the dispersion of carbon black. During carbon black incorporation and dispersion high shearing action

Table 4—Effect of mixing on polymer molecular weight and carbon black dispersion

	Formulation number							
	1	2	3	4	5	6	7	8
$\bar{M}_n \times 10^{-5}$	1.23	1.25	—	1.47	—	—	1.70	1.75
Variance ( $\sigma^2$ ), MPa								
200% Modulus	0.135	0.146	0.098	0.089	0.036	0.107	0.027	0.031
300% Modulus	0.181	0.202	0.136	0.148	0.084	0.107	0.075	0.065
Tensile strength	0.532	0.745	0.282	0.287	0.382	0.487	0.246	0.263

Table 5—Effect of modified carbon black on curing behaviour in SBR vulcanizates

Monsanto rheometer R-100 data at 150°C	Formulation number							
	1	2	3	4	5	6	7	8
Optimum cure time, min	27	27	27	27	31	32	32	32
Scorch time, min	7	7	7	7.5	7.5	7.5	8.0	8.0
Extent of cure, dNm	58	60	56	54	57	52	56	59.5
Cure rate index, min <sup>-1</sup>	5.0	5.0	5.0	5.1	4.3	4.1	4.2	4.2

Table 6—Effect of modified carbon black on mechanical properties of SBR vulcanizates

Vulcanizate properties	Formulation number							
	1	2	3	4	5	6	7	8
200% Modulus, MPa	5.9	5.8	4.4	4.5	3.5	3.5	4.1	4.2
300% Modulus, MPa	11.3	11.8	8.6	8.5	8.9	7.5	8.8	8.6
Ten. strength, MPa	19.4	19.7	18.0	18.9	19.0	18.0	20.3	20.4
Elong. at break, %	420	400	450	460	465	510	505	500
Hardness, Shore A	72	72	66	66	68	66	67	67
Bound rubber, %	30.9	31.0	26.5	26.6	25.0	23.2	25.0	25.2
Heat build up, °C	28	28	26	26	27	29	29	30
Flex-cracking resistance, k cycles	28	30	44	43	44	55	82	84
Abrasion loss, % in 1000 cycles	1.23	1.14	1.32	1.36	1.27	1.47	0.96	0.89
Swelling value, $\rho$	2.93	2.95	3.32	3.33	3.41	3.53	3.82	3.89

causes polymer chain scission and increases the temperature of the mix<sup>23</sup>. The decrease of viscosity of the mix due to chain scission and temperature rise, causes plasticization around carbon black agglomerates and thus retards the dispersive mixing<sup>24-26</sup>. Moreover, use of process oil for the dispersive mixing affects the tensile properties in general<sup>27</sup>. The temperature rise during mixing is shown in Fig. 1. The results show the higher temperature rise in the formulations 1 and 2 compared to formulations 7 and 8. The formulations 3 and 4 containing spindle oil as processing aid and the formulations 5 and 6 showed intermediate temperature rise.

Formulations containing modified carbon black (formulations 7 and 8) showed the lowest chain scission and the formulations 1 and 2 showed the highest chain scission as evident by viscosity average molecular weight (Table 4). Formulation 4 with process oil showed intermediate chain scission. The relatively lower value of variance ( $\sigma^2$ ) for modified black formulations supported the uniformity of carbon black dispersion in the rubber

phase. These observations indicate better processing behaviours and uniformity in ultimate properties offered by modified carbon blacks over those of control.

*Cure characteristics*—Cure characteristics are presented in Table 5. From the results it is evident that either the presence of acid as processing aid (formulation 5) and as simple physical mixture with carbon black or the acid modified carbon blacks (formulations 7 and 8) has marginally increased the optimum cure time and scorch time which are quite normal observations, since cure rate decreases in acidic environment. However, modification does not affect the extent of cure to a considerable extent.

*Tensile properties*—Table 6 shows the tensile properties of all the formulations containing modified and unmodified carbon blacks. Both 200% and 300% moduli have changed a little due to the modification. In the formulations 7 and 8 containing modified carbon blacks, the moduli values remained almost in the same level as those of the formulations 3 and 4. But the formulations 1 and 2 where no oil was used during mixing show the comparatively

higher moduli. The relative higher value of 200% and 300% moduli in these formulations are due to the higher effective volume of loading (45 phr) and without process oil. These make the sample more stiff, which is reflected in the enhanced value of hardness<sup>28</sup>. The tensile strength values of formulations 7 and 8 containing modified carbon blacks are improved over that of the control formulations. But the formulation 5 where the acid (modifying agent) is used as processing aid and the formulation 6 where the acid is present in a simple physical mixture do not show significant improvements of the above mechanical properties. However, it is worth mentioning that modification of carbon black with the organic acid is associated with the improvement of the ultimate properties.

The value of percentage elongation at break (Eb%) is also presented in Table 6. Formulations 7 and 8 show higher values of Eb% than formulations 1 to 5. Higher values of Eb% in formulations 7 and 8 indicate higher flex fatigue life of the sample<sup>29</sup>. Formulation 6 (modifying acid is in simple physical mixture with carbon black) also shows an enhanced Eb% value. These results are also the indication of the higher flexibility offered by the modifying acid present as a simple physical mixture with carbon black.

*Bound rubber*—The effect of modification of carbon black with the organic fatty acid was also tested by measuring the bound rubber content. The results are included in Table 6. It is evident from the results that the modified carbon blacks (formulations 7 and 8) slightly lower the bound rubber content compared to the control compounds (formulations 3 and 4). This lowering of bound rubber is probably due to the decrease of surface area and DBP structure of carbon black after modification with the organic fatty acid. Since the bound rubber gives a measure of reinforcement<sup>30</sup> and is a function of surface area and structure<sup>31</sup> it is prominent that formulations 1 and 2 without process oil show around 5% higher bound rubber content than that of the formulations 3 and 4 with process oil. This phenomenon again can be understood on the basis of higher carbon black content in formulations 1 and 2 having no process oil.

*De Mattia crack growth and abrasion resistance*—Since carbon black filler plays an important role on fatigue flex life<sup>32</sup> De Mattia crack growth resistance of both modified and unmodified black filled stocks was measured (Table 6). It is

interesting to observe that the crack growth resistance value is quite higher in the formulations 7 and 8 containing modified black compared to all other formulations (Table 6). Although the flex cracking resistance is also a function of crosslinking system used<sup>33,34</sup>, the higher value of crack growth resistance in formulations 7 and 8 is believed to be due to the attachment of the flexible chain of the fatty acid to the carbon black surface.

This modified carbon black is assumed to provide a flexible bridge between the filler surface and the elastomer matrix thereby relieving the localized stresses generated during flexing operation, thus resulting in an improvement of flex life<sup>35,36</sup>. The moderately higher values of flex cracking resistance in formulations 3 to 6 compared to the formulations 1 and 2, are due to the presence of process oil and modifying agent as physical mixture with carbon black.

In respect of abrasion resistance modified carbon black filled elastomer shows much improved results of abrasion resistance compared to unmodified control stocks (compare formulations 7 and 8 with formulations 1 to 4). Many workers have shown better abrasion resistance after modification of carbon black with various agents in different elastomeric systems<sup>15,37,38</sup>. In our study the improvement of abrasion resistance is probably due to the presence of chemically bound organic acid as a bridge between the carbon black and the elastomer which resists the polymer to be abraded out of the system. The higher abrasion losses in the formulations 3 to 6 are believed to be due to the presence of oil which may be responsible for polymer dilution and thus increases the loss during abrasion<sup>39</sup>.

*Goodrich heat build up*—Goodrich heat build up values (in terms of temperature rise in degree centigrade) is presented in Table 6. It is seen that the formulations 7 and 8 show a little higher heat build up than that shown by other unmodified black filled (control) stocks, (formulations 1 to 4). Heat build up is related to bound rubber characteristics which is also related to the carbon black rubber interaction density. In the present investigation, vulcanizates containing modified carbon black (formulations 7 and 8) showed lower bound rubber content and higher heat build up characteristics. This is in good agreement with the findings of Fabre and Bertrand<sup>40</sup> who showed decrease of heat build up with increase of bound rubber by attaching chemical promoters to

carbon black. The relation of heat build up and bound rubber may be explained as follows. Lower polymer carbon interaction and hence lower bound rubber may be regarded as longer folded/coiled polymer chain segments between two points of interaction. Application of cyclic stress generates frictional heat due to unfolding/folding of such coiled segments and consequently longer chain segments will generate more heat. Moreover, it is known that heat generation is associated with the crosslinking system<sup>41</sup>. Decrease in the crosslink density causes higher heat generation<sup>42</sup>. The swelling value ( $Q$ ) of the cured samples (Table 6) is taken as a measure of the total crosslink density of the vulcanizates. Higher values of  $Q$  in case of formulations 7 and 8 indicate establishment of lower crosslink densities (interaction density) in them. The loosely crosslinked system is partially responsible for relatively higher heat build up in the modified black formulations. Slightly higher swelling values ( $Q$ ) for formulations 3 and 4 compared to those for formulations 1 and 2 are due to spindle oil used as processing aid. The most densely cured samples showing the lowest  $Q$  value, formulations 1 and 2, showed heat build up that is higher than that for formulations 3 and 4. This can be attributed to the effective higher loading without the use of process oil.

### Conclusion

The present investigation on the behaviour of modified carbon black to the tensile and dynamic properties of rubber vulcanizates indicates better flex crack growth resistance and abrasion resistance with improved balance of tensile properties thus making the vulcanizates much suited for tyre applications.

### Acknowledgement

The authors thankfully acknowledge Birla Tyres, India for providing the facilities of heat build up measurement of rubber samples.

### References

- Donnet J B & Henrich G, *J Polym Sci*, 46 (1960) 277.
- Donnet J B, Henrich G & Riess G, *Rev Gen Caout Plast*, 41 (1962) 583.
- Donnet J B, Geldreich L, Henrich G & Riess G, *Rev Gen Caout Plast*, 41 (1964) 519.
- Donnet J B, Peter G & Riess G, *J Polym Sci*, 22 (1969) 645.
- Donnet J B, Vidal A, Riess G & Geldreich L, *Rev Gen Caout Plast*, 47 (1970) 1289.
- Donnet J B, Vidal A & Riess G, *Paper presented at IUPAC Int Symp on Macromolecular Chem*, Budapest, 25-30 August, 1969.
- Vidal A, Ph.D. Thesis, Faculty of Science, University of Strasbourg, France, July 1970.
- Dannenberg E M, Papirer E & Donnet J B, *Rev Gen Caout Plast*, 51 (1974) 823.
- Dannenberg E M, Papirer E & Donnet J B, *Colloq Int CNRS*, 231 (1975) 121.
- Vidal A, Hao S Z & Donnet J B, *Kaut Gummi Kunstst*, 44 (1991) 419.
- Wang W D, Vidal A, Nanse G & Donnet J B, *Kaut Gummi Kunstst*, 47 (1994) 493.
- Rivin D & Dannenberg E M, *Unpublished work*, 1970. Reference 53 in Dannenberg E M, *Rubber Chem Technol*, 48 (1975) 410.
- Furukawa J, Yamashimo S, Shimori J & Kotani T, *Japan Pat.* 7120, 886 (1971).
- Henkel und Cie, *G.m.b.H. Fr. Demande*, 2, 012, 296 (1970).
- Takino H, Hatsumoto H, Okamura A, Tomokuni H & Oda K, *Jpn Kokai Tokkyo Koho JP*, 6366, 247 (1988).
- Gajewski M & Prot T, *Kaut Gummi Kunstst*, 47 (1994) 574.
- Adhikari B, *J Polym Mater*, 9 (1992) 175.
- Ghosh A K, Adhikari B & Maiti S, *J Polym Mater*, 12 (1995) 285.
- Brennan J J, Jermyn T E & Boonstra B B, *J Appl Polym Sci*, 8 (1964) 2687.
- Parks C R & Brown R J, *Rubber Chem Technol*, 49 (1976) 233.
- Studebaker M L, *Rubber Chem Technol*, 30 (1957) 1400.
- Bansal R C, Donnet J B & Stoeckli F, *Active Carbon*, (Marcel Dekker, New York), 1988.
- Johnson P S, in *Rubber Products Manufacturing Technology*, ed. by A K Bhowmik, M M Hill & H A Benary, (Marcel Dekker, New York), 1994, 108.
- Freakley P K & Patel S R, *Rubber Chem Technol*, 58 (1985) 751.
- Edmondson H M, *Inst Rubber Ind Conference*, April 1969.
- Bourne J R, *New Scientist*, 33 (1967) 334.
- Hess W M, Swor R A & Micek E J, *Rubber Chem Technol*, 57 (1984) 959.
- Byers J T, *Rubber World*, 189 (1983) 26.
- Conant F S, in *Rubber Technology*, ed. by M Morton, (Van Nostrand Reinhold, New York), 1986, 146.
- Stickney P B & Falb R D, *Rubber Chem Technol*, 37 (1964) 1299.
- Brennan J J & Jermyn T E, *J Appl Polym Sci*, 9 (1965) 2749.
- Dizon E S, Hicks A E & Chirico V E, *ACS Rubb Div Mtg Denver*, (1973), paper No. 23.
- Bateman L, *The Chemistry and Physics of Rubber Like Substances*, (MacLaren, London), 1963.
- Campbell D S, *J Appl Polym Sci*, 14 (1970) 1409.
- Cooper W, *J Polym Sci*, 28 (1958) 195.
- Dogadkin B A, Tarasova Z N & Goldberg I I, *Proc Rubber Technol Conf*, 4th, London, 1962, (1963) 65.
- Kurimoto I, Yamaguchi T, *Jpn Kokai Tokkyo Koho JP*, 01, 275, 666 (1989).
- Belmount J A & Funt J M, *Kaut Gummi Kunstst*, 44 (1991) 1135.
- Byers J T, in *Rubber Technology*, ed. by M Morton, (Van Nostrand Reinhold, New York), 1987, 83.
- Fabre R & Bertrand G, *Rev Gen Caout Plast*, 42 (1965) 405.
- Kempermann T, *Rubber Chem Technol*, 55 (1982) 391.
- Meinecke E, *Rubber Chem Technol*, 64 (1991) 269.