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The Vulcanization Characteristics and Physical Properties of Carbon Black Loaded–Polymeric Composites: I. N-220 Black Loaded PVC/EPDM Composites

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Abstract In the present study, attempts have been made to modify carbon black filled Ethylene-propylene-diene monomer (EPDM) /Poly vinyl chloride (PVC) composites. Compounding were carried out using a two-roll mill and vulcanized at 145℃. The modified blend of unfilled PVC/EPDM was characterized on the basis of the effect of PVC ratio on curing parameters, mechanical and swelling properties of blends were investigated. The effect of N220 black content on vulcanization characteristics and mechanical properties of 80PVC/20EPDM composites were also examined. The minimum torque and maximum torque of the blend increased by increasing N220 black content in CB filled PVC/EPDM blend. Scorch time, cure time, elongation at break decreased after increasing of N220 content, but tensile strength, hardness and specific gravity increased. Overall, an observed enhancement in curing parameters and mechanical properties have been achieved by incorporating N220 black into the unfilled PVC/EPDM composites.

Keywords Vulcanization characteristics, N220 black, Filled PVC/EPDM blend

1. Introduction

Rubbers became highly important industry due to its various applications, such as cables and tires. This is because of their light weight, high flexibility, hydrophobicity, low cost and easy manufacturing. The incorporation of filler into a polymer enhances the mechanical properties of the final product, and also decreases the cost of the end product. The carbon black may be introduced as a filler in rubber in the form of aggregations [1,2]. In addition, filling carbon black increases the reinforcement of vulcanized rubber [1,3] and also enhances physical properties of the polymeric matrices [4,5]. The entanglement of rubber molecules that linked the carbon black surface is very important for the construction of rubber -carbon black matrix [6]. Park et al. studied the effect of surface energy of carbon blacks on the mechanical properties of carbon black/rubber composites [7-9]. They concluded that, the addition of black filler increases the vulcanization reactions and enhances the mechanical properties of the composites [8]. Scanning electron microscope (SEM) is a technique used to give a full description of the filled rubber [10,11]. Also, the incorporation of ethylene-propylene-diene rubber (EPDM) to carbon blacks was studied by using nuclear magnetic resonance (NMR) [12]. They found the rubber molecule complete mixed with the carbon black surface and the reinforcement increases. Poly vinyl chloride (PVC) is a versatile polymer, used in flexible, semirigid, and rigid forms. The rapid consumption of PVC is due to lower cost, greater availability, good mechanical properties, and diversity of its properties [13,14]. One of the most prominent needs for PVC in application end use is permanent plasticization. A very important and commercially significant blend is that of NBR and PVC. NBR acts as a permanent plasticizer for PVC, and at the same time PVC improves the ozone, thermal ageing, and chemical resistance of NBR. The presence of PVC improves aging resistance of NBR as both PVC and NBR are polar and blending NBR with PVC increases the compatibility [15,16]. Triazine trithiols can be used as a co-crosslinking agent for PVC/EPDM blends [17-19]. Properties of PVC/EPDM blends modified with chlorinated polyethylene (CPE) were also investigated [20]. The present work is a useful technique for producing polymer composites based on plasticized PVC and EPDM rubber filled with different conductive carbon blacks and testing their characteristics. We compare the cure characteristics and mechanical properties of the polymeric matrix in order to study the effect of the structure of the

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carbon black on the carbon black loaded PVC /EPDM composites.

2. Experimental Procedures

Materials

The following raw materials were used:

(1) EPDM rubber (with 54% ethylene content) was donated from Transportation and Engineering Co., (TRENCO, Alexandria, Egypt).
(2) Plasticized PVC prepared from PVC with a 67 value, dioctylphthalate (DOP), PVC Stabilizer and antioxidant.
(3) The carbon black used in this work is N220 (ISAF) from CARBON BLACK Co., Egypt.
(4) Other chemicals such as zinc oxide, stearic acid, tetra methyl thiuram disulphide (TMTD), paraffinic oil and peroxide were used in commercial grades without purification and locally manufactured by ADWIC Co., Egypt.

Blend Preparation

Five formulations of PVC/EPDM Composites were carried out according to ASTM D 3185 – (99). All the rubber ingredients were accurately supplied, weighed and mixing on a laboratory mill at TRENCO Company, Alexandria, Egypt, with the following dimensions: diameter 460 mm, working distance 250 mm, speed of the slow roll 16 rpm and gear ratio 1.4. The mill has the facility of rolling temperature control. The blend compositions are listed in Table 1. The optimum curing time was obtained by using MDR-2000 rheometer. Before all tests, all rubber blends were vulcanized using a hot press at 143 ± 2 ℃ for 10 minutes by means of standard dies in accordance with ASTM D-3191 standard.

Table 1. Recipe of PVC/EPDM composites

Sample ratio PVC/EPDM	Chemicals Additives (phr*)					
	ZnO	Stearic Acid	paraffinic Oil	DOP	TMTD	Peroxide
0/100	5	2	25	---	3	4
20/80	5	2	20	5	3	4
40/60	5	2	15	10	3	4
60/40	5	2	10	15	3	4
80/20	5	2	5	20	3	4

* Part per hundred parts of rubber by weight

The optimum value which obtained from Table 1 was used and loaded with different ratios of carbon black N220 as shown in Table 2.

Mechanical properties

The mechanical properties of unfilled and filled PVC/EPDM Composites were measured on a Monsanto tensometer of capacity 10 kN according to ASTM D-412 at room temperature. Specimens prepared by cutting three individual dumbbell shape specimens from the polymeric samples by a steel die of constant width (4 mm) between the two dumbbells.

Table 2. Recipe of carbon black-loaded 80PVC/20EPDM composites

Sample ingredients (phr)	S0	S20	S40	S60	S80	S100
PVC	80	80	80	80	80	80
EPDM	20	20	20	20	20	20
ZnO	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
Paraffinic oil	5	5	5	5	5	5
DOP	20	20	20	20	20	20
N220 black	---	20	40	60	80	100
TMTD	3	3	3	3	3	3
Peroxide	4	4	4	4	4	4

Physicochemical properties (Swelling measurements)

Strips of dimensions 0.2x0.5 x 2 cm^3 were immersed in benzene at room temperature for 24 hours. The maximum degree of swelling is measured using the following relation

$$Q_m(\%) = \frac{M_s - M_d}{M_d} \times 100 \quad (1)$$

where M_s and M_d are the masses of swell and dry piece of rubber, respectively. The mass of the sample was measured by electronic digital balance of 0.001 gm accuracy.

3. Results and Discussion

Effect of PVC content on the vulcanization characteristics and mechanical properties of PVC/EPDM blends

Vulcanization characteristics

Table 3 summarizes the rheological characteristics of EPDM/PVC blends. The obtained data show that the increase of PVC content results in an increase of minimum torque (M_L) and maximum one (M_H). In other words, M_L which reflects the minimum viscosity of the blends is affected by the increasing amount of PVC content. This is due to PVC is polar that increases the polarity which results in more interaction between two phases of polymer matrix. These results are in good agreement with the obtained results of K. Ahmed et al. [21]. Furthermore, the dependence of the optimum cure time (T_{90}) and scorch time (T_{sc}) is observed. The decreasing trend may be attributed to the presence of PVC content in blends, which increases the reactive sites, decreases the time for cross linking in rubber blends.

The cure rate index (CRI) is a measure of the rate of vulcanization [22] which based on the difference between optimum vulcanization time as follows:

$$CRI = \frac{100}{T_{90} - T_{sc}} \quad (2)$$

The calculated values of CRI are also presented in Table 3. It is noticed that CRI decreases with increasing of PVC content in PVC/EPDM blend. This indicates that PVC as a polar in nature is a cure activating compound in various PVC/EPDM blends and increases the activating sites for vulcanization.

Table 3. The curing parameters of PVC/EPDM blends

Blend Ratio	M_L (dNm)	M_H (dNm)	T_{90} (min)	T_{sc}(min)	CRI
0PVC/100EPDM	0.82	1.02	2.89	1.83	98.94
20PVC/80EPDM	0.95	1.5	2.76	1.34	70.42
40PVC/60EPDM	1.45	6.7	2.33	1.22	90.09
60PVC/40EPDM	3.56	13.3	1.87	0.68	84.034
80PVC/20EPDM	4.5	24.5	1.74	0.53	82.64

Mechanical properties and Physico-chemical properties

Table 4. The mechanical parameters of PVC/EPDM blends

Blend Ratio	TS (MPa)	E_b (%)	Hardness (Shore A)	Sp. Gr.	Q_{max} (%)
0/100	0.8	1.072	34.8	1.25	244
20/80	1.2	1.1	35.2	1.28	198
40/60	1.6	1.45	37.3	1.31	166
60/40	2.5	1.73	38.5	1.33	94
80/20	2.8	1.854	38.95	1.39	82

The mechanical properties, in terms of tensile strength, elongation at break, hardness and specific gravity were determined for PVC/EPDM blends and the results were tabulated in Table 4. The marked increase of tensile strength (TS) may be attributed to the increase in PVC content which lead to a strong dipole-dipole interaction between PVC and EPDM molecules. In addition, the higher strength and lower elongation may be owed to the increase of the cross-linking density which is in good agreement with the curing parameters results. The hardness of PVC/EPDM blends are comparatively higher compared to same blends prepared with sulfur as curing agent. This may be due to the curing of EPDM phase in the presence of peroxide as curing agent. Comparing the specific gravities of PVC (~1.4) and EPDM (~1.25); the increase of the specific gravity with increasing PVC content (see Table 4), verifies pretty well the law of mixing. It is expected that the blends possess intermediate Sp. Gr. values between those of EPDM and PVC values. A decreasing trend could be observed for the values of degree of swelling in benzene (Q_{max} (%)) against PVC content. The marked decrease of Q_{max} (%) may be attributed to the decrease of volume fraction of the amorphous swollen phase (EPDM) by increasing the crystalline phase (PVC). An overall enhancement in mechanical parameter of PVC/EPDM blends should be observed as the existence of good interfacial adhesion of PVC/EPDM blends.

Effect of N220 black content on the vulcanization characteristics and mechanical properties of 80PVC/20EPDM blend

Vulcanization characteristics

The cure characteristics of N-220 filled 80PVC/20EPDM blends are shown in Table 5, where α is defined as:

$$\alpha = \frac{M_H - M_{H0}}{M_{H0}} \tag{3}$$

where M_H and M_{Ho} are the maximum torque of filled matrix and gum vulcanizates samples, respectively. It is noticed that, the values of M_L, M_H and α increase by increasing N220 content for rubber compounds. This is due to the fact that EPDM chains contact with carbon black particles and entangle or trap in the voids between carbon black particles or aggregates [23]. In other words, α is defined as the relative increase of M_H upon increasing of N220 content. The increasing trend of the previous parameters could be attributed to the fact that N220 increases the formation of aggregations which have characteristic weak physical bond which lead to a breakdown of the structure of carbon black. It is seen that CRI increases with N220 addition and a maximum value is observed at certain concentration of carbon black (60phr) and then started to decrease again due to the ease break down of carbon black structure with extra loadings of black concentration [24,25]. Finally, T_{90} and T_{sc} decrease with increasing N220 content. This is due to the increasing of crosslinking density due to the increase of carbon black concentrations in the polymer matrix.

The ratio between the change in torque, M, of the filled compound and that of the gum is given as follows [26]:

$$\frac{M_H - M_L}{M_{H0} - M_{L0}} - 1 = \alpha_f \frac{m_f}{m_r} \tag{4}$$

where $M_H - M_L$ is the maximum change in torque during the vulcanization process for filled blend, $M_{H0} - M_{L0}$ is the maximum change in torque during the vulcanization for the gum vulcanizates, m_r is the mass of the rubber in the matrix, m_f is the mass of the filler in the same matrix and α_f is a filler constant that independent of the matrix and related to the morphology of the filler [27,28].

Table 5. The Curing parameters of N220 black filled 80PVC/20EPDM blends

Blend Ratio	N220 Content (phr)	M_L (dNm)	M_H (dNm)	T90 (min)	Tsc (min)	$\alpha \times 10^{-2}$	CRI min^{-1}
80PVC/20EPDM	0	1.23	6.34	3.12	1.81	0	76.3
	20	2.34	7.36	2.34	1.12	16	81.97
	40	3.44	11.98	1.76	0.8	41	104.17
	60	6.82	16.78	1.34	0.66	164.7	147.1
	80	8.81	23.22	1.31	0.51	266.2	125
	100	9.2	23.56	1.21	0.35	271.6	116.3

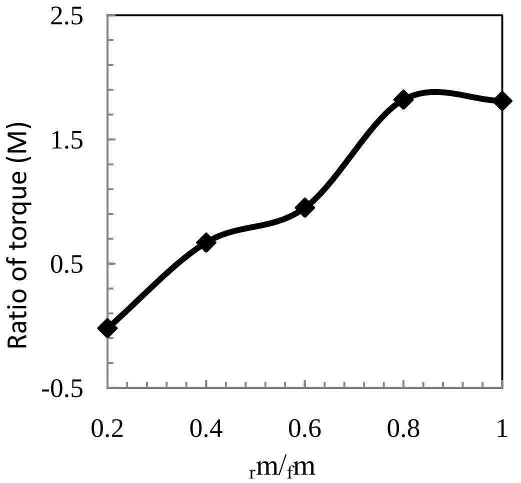

Figure 1. Variation of ratio of torque, M, as a function of N220 loading for filled 80PVC/20EPDM blend

From the data of Fig. 1, it is clear that M increases with increasing N220 content up to 80 phr and this could be considered as the optimum concentration which resulted in a better interfacial interaction between rubber and filler in the polymeric matrix.

Mechanical properties

The effect of N220 loadings on the mechanical properties of 80PVC/20EPDM blends is presented in Figs. (2-5). It is clear that TS increased with increasing N220 content due the reinforcement of CB to the rubber matrix (Fig. 2). While at higher filler loadings, the tensile strength is decreased again due to the weak Vander Walls forces between the excess carbon black particles and/or aggregates. As a result of these competitions, a peak value is observed at 60 phr of N220 black content.

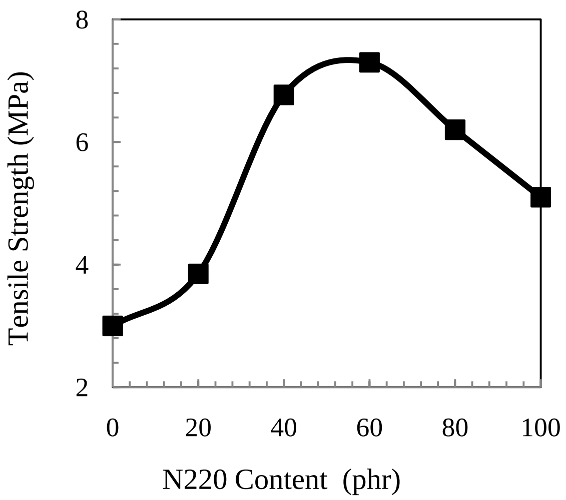

Figure 2. The variation of tensile strength against filler loading for 80PVC/20EPDM blend

E_b shows a decreasing trend upon N220 loadings for all samples (Fig. 3). This is due to the reinforcing process upon black addition.

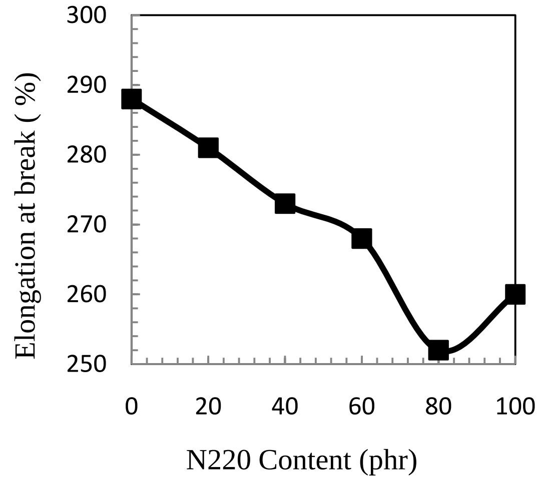

Figure 3. Elongation at break versus N220 content for 80PVC/20EPDM blend

Fig. 4 illustrates the increasing trend of the shore hardness values which could be attributed to the increase of the harder phase (CB) in the soft polymeric matrix.

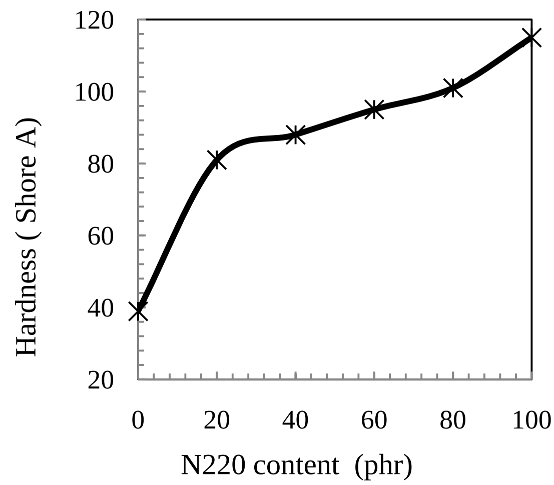

Figure 4. Effect of N220 black content on shore hardness values of 80PVC/20EPDM blend

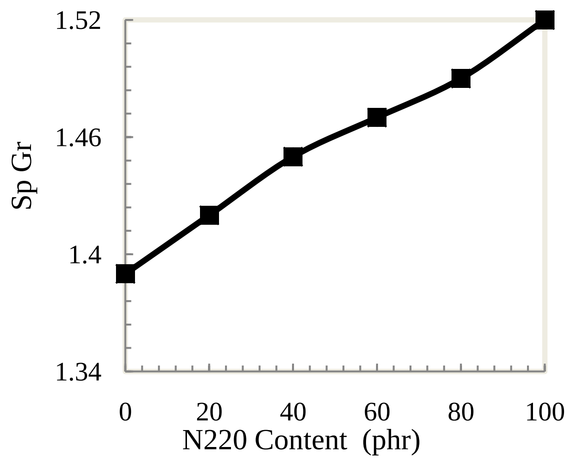

Figure 5. Effect of N220 black content on the specific gravity values of 80PVC/20EPDM blend

Comparing the specific gravities of EPDM (~1.25) and that of carbon black (~1.82). The increase of the specific gravity upon increasing carbon black content, Fig. 5, verify pretty well the law of mixing.

Table 6 describes the reinforcing index (RI) values of 80PVC/20EPDM blend sample which is an empirical parameter representing reinforcement effect on a mechanical property [29], and is given by the following relation:

$$RI = \frac{1}{V_B} \times \left(\frac{\sigma_2}{\sigma_1}\right) \tag{5}$$

where σ_1 and σ_2 are the tensile strength for pure and filled blend, respectively and V_B is the volume fraction of N220 black content.

Table 6. RI values of filled 80PVC/20EPDM blend

Sample name	N220 (phr)	Reinforcement Index (RI)
80PVC/20EPDM	0	-----
	20	11.55
	40	11.28
	60	7.3
	80	4.75
	100	3.1

4. Conclusions

From the results obtained, the cure characteristics and mechanical properties of pure PVC/EPDM blends depends on PVC content. N220 filled 80PVC/20EPDM blend samples tend to reduce scorch time, cure time and elongation at break but minimum torque, maximum torque and hardness shows the opposite trend with increasing N220 black content in N220 filled 80PVC/20EPDM blend samples. While tensile strength of the blend first increases and then decreases. The filler addition much influenced on CRI and RI values. Finally, this study shows that the optimum blend, 80PVC/20EPDM can be used for the low cost of the final product in industrial applications due to a marked enhancement in both curing and mechanical parameters of the final blend.

REFERENCES

[1] F. R. Eirich, Science and technology of rubber, Academic Press, New York (1978).

[2] A. Zhang, L. Wang, Y. Lin and X. Mi, Carbon black filled powdered natural rubber: Preparation, particle size distribution, mechanical properties, and structures, Journal of Applied Polymer Science, 101, 1763–1774 (2006).

[3] M. S. Khan, D. Lehmann and G. Heinrich, Modification of PTFE nano powder by controlled electron beam irradiation: A useful approach for the development of PTFE coupled EPDM compounds, Express Polymer Letters, 2, 284–293 (2008).

[4] D. Pantea, H. Darmstadt, S. Kaliaguine and C. Roy, Electrical conductivity of conductive carbon blacks: Influence of surface chemistry and topology, Applied Surface Science, 217, 181–193 (2003).

[5] D. Pantea, H. Darmstadt, S. Kaliaguine and C. Roy, Heat treatment of carbon blacks obtained by pyrolysis of used tires, Effect on the surface chemistry, porosity and electrical conductivity. Journal of Analytical and Applied Pyrolysis, 67, 55–76 (2003).

[6] G. Heinrich and T. A. Vilgis, Contribution of entanglements to the mechanical properties of carbon black filled polymer networks. Macromolecules, 26, 1109–1119 (1993).

[7] S-J. Park and J-S. Kim, Role of chemically modified carbon black surfaces in enhancing interfacial adhesion between carbon black and rubber in a composite system, Journal of Colloid and Interface Science, 232, 311–316 (2000).

[8] S-J. Park, M-K. Seo and C. Nah, Influence of surface characteristics of carbon blacks on cure and mechanical behaviors of rubber matrix compounding, Journal of Colloid and Interface Science, 291, 229–235(2005).

[9] S-J. Park, K-S. Cho and S-K. Ryu, Filler-elastomer interactions: Influence of oxygen plasma treatment on surface and mechanical properties of carbon black/rubber composites, Carbon, 41, 1437–1442 (2003).

[10] J. H. Wang, G. Z. Liang, H. X. Yan and S. B. He, Mechanical and dielectric properties of epoxy/dicyclopentadiene bisphenol cyanate ester/glass fabric composites, Express Polymer Letters, 2, 118–125 (2008).

[11] A. Das, R. Jurk, K. W. Stöckelhuber and G. Heinrich, Rubber curing chemistry governing the orientation of layered silicate, Express Polymer Letters, 1, 717–723 (2007).

[12] V. M. Litvinov, P. A. M. Steeman, EPDM-carbon black interactions and the reinforcement mechanisms, as studied by low-resolution 1H NMR, Macromolecules,32, 8476–8490 (1999).

[13] W. V. Titow, PVC Technology, Ch. 2, Elsevier Applied Science Publishers, 4th edition, 1984.

[14] D. Braun and E. Bezdadea, “Encyclopedia of PVC” L. I. Nass and C. A. Heiberger, Eds., Ch. 1, (1986).

[15] V. L. D. C. Lapa, L. L. Y. Visconte, J. E. D. S. Affonso, and R. C. R. Nunes, “Aluminum hydroxide and carbon black filled NBR/ PVC composites—vulcanization and processability studies,” Polymer Testing, 21(4), 443–447 (2002).

[16] J. Thormer, H. Bertram, O. Benn, and H. Hurrnik, “Use of zinc salts of mercaptobenzimid azole and dithiophosphoric acid esters for the preparation on nitrile rubber/poly (vinyl chloride) mixture, U.S. Patent, no. 4, 435–532(1984).

[17] Y. Nakamura, K. Mori and R. Takesawa, Int. Polym. Sci. Technol, 7 (7), T/9 (1980).

[18] K. Mori and Y. Nakamura, plast. Rubb. Process. Appl., 3 (1), 17 (1983).

[19] Y. Nakamura, K. Mori, R. Takesawa and M. Saito, Int. Polym. Sci. Technol., 7 (2), T/89 (1980).

[20] Y. D. Lee and C. M. Chen, J. Appl. Polym. Sci., 33 (4), 1231 (1987).

[21] K. Ahmed, S. Nizami, N. Raza and K. Shirin, “Curing characteristics, mechanical and swelling properties of marble sludge filled EPDM modified chloroprene rubber blends”, Adv. Mat. Phys. Chem., 2, 90-97 (2012).

[22] A. Aprem, S. Jose, S. Thomas, N. Barkoula and J. Kocsis, Eur. Polym. J., 39, 69 (2003).

[23] Z. Li, J. Zhang and S. Chen, Effects of carbon blacks with various structures on vulcanization and reinforcement of filled ethylene-propylene-diene rubber, Express polymer letters, 2 (10), 695-704 (2008).

[24] R. Norman, Conductive rubbers and plastics, Appl. Sci. Publ. Ltd., London (1970).

[25] E. Abdel-Bary, M. Amin and H. Hassan, J. Polym., Polym. Chem. Ed., 17, 2163 (1979).

[26] M. Sobhy, D. El-Nashar and N. Maziad, Cure characteristics and physicomechanical properties of calcium carbonate reinforcement rubber composites Egypt J. Sol., 26 (2), (2003).

[27] S. Wolff and M-J. Wang, Rubber Chem. Technol., 65, 329 (1992).

[28] S. Wolff, Rubber Chem. Technol., 73,524 (2000).

[29] S. Kohgiya and Y. Ikeda, Rubber Chem. Technol., 73, 534 (2000).