

THE EFFECT OF RUBBER MIXING PROCESS ON THE CURING CHARACTERISTICS OF NATURAL RUBBER

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Abstract

This research is aimed at studying the relationship between rubber mixing processes and curing characteristics of natural rubber. The curing characteristic analysis was carried out through a natural rubber formula having been masticated and mixed, followed by curing. As many as four mastication methods were finely applied; each respected four sequences of rubber mixing process. In the first method, rubber was masticated for 5 minutes and then rubber chemicals and carbon black N 330 were simultaneously added. In the second and the third methods, rubber was masticated for 1 minute and then carbon blacks and rubber chemicals were also simultaneously added but using different type of fillers. In the fourth method, rubber was masticated for 3 minutes and then rubber chemicals and carbon black were subsequently added. The additions of rubber chemicals and carbon blacks to the masticated rubber were distinguished by the sequence and time allocated for each mixing process. The carbon blacks were added in two stages by which 10 phr was added first and the remaining 40 phr was added later along with oil. In another method, ratios of the carbon blacks addition (as done in the first and the second stages) were 20:30, 30:20, and 40:10. The examination results showed that rubber mixing process gave an impact on the changes of curing characteristics. They were much affected by the method of carbon black addition. The mixing temperature also had an effect on both curing time and curing rate in which the higher the mixing temperature, the lower the curing time and curing rate. Vulcanization temperature also affected the curing time and curing rate in which the higher the vulcanization temperature, the lower the curing time and the higher the curing rate. Lastly, particle size of carbon black also gave an impact on the curing time and curing rate in which the smaller the particle size, the lower the curing time and the higher the curing rate.

Abstrak

Pengaruh Proses Penggilingan Karet terhadap Karakteristik Vulkanisasi Karet Alam. Tujuan penelitian ini adalah untuk mempelajari hubungan antara proses penggilingan karet dan karakteristik vulkanisasi karet alam. Analisis karakteristik vulkanisasi dilakukan dengan merancang formula karet alam yang dimastikasi dan digiling, kemudian diikuti dengan pengamatan reaksi vulkanisasi. Ada empat metode mastikasi yang masing-masing metode diikuti oleh empat urutan proses pencampuran karet. Metode pertama, karet dimastikasi selama 5 menit dan kemudian diikuti penambahan bahan kimia karet dan *carbon black* N 330 secara simultan. Metode kedua dan ketiga, karet dimastikasi selama 1 menit kemudian *carbon black* dan bahan kimia karet ditambahkan secara simultan tetapi menggunakan bahan mengisi dengan tipe yang berbeda. Metode keempat, karet dimastikasi selama 3 menit dan kemudian *carbon black* ditambahkan dahulu lalu diikuti dengan penambahan bahan kimia karet. Penambahan bahan kimia karet dan *carbon black* ke dalam karet dibedakan atas urutan dan waktu yang dibutuhkan untuk masing-masing proses pencampuran. *Carbon black* ditambahkan dalam dua kali, yang pertama 10 phr ditambahkan kemudian sisa *carbon black* 40 phr ditambahkan kemudian bersamaan dengan penambahan minyak. Metode yang lain, nisbah penambahan *carbon black* (penambahan pertama dan penambahan kedua bersamaan dengan minyak) adalah 20:30, 30:20, dan 40:10. Hasilnya menunjukkan bahwa proses penggilingan karet mempengaruhi perubahan karakteristik vulkanisasi. Ini dipengaruhi oleh metode penambahan *carbon black*. Suhu penggilingan juga mempengaruhi waktu dan laju vulkanisasi, di mana semakin tinggi suhu penggilingan, semakin rendah waktu dan laju vulkanisasi. Suhu vulkanisasi juga mempengaruhi waktu dan laju vulkanisasi dengan semakin tinggi suhu vulkanisasi, semakin rendah waktu vulkanisasi dan semakin tinggi laju vulkanisasi. Selanjutnya, ukuran partikel *carbon black* juga mempengaruhi waktu dan laju vulkanisasi di mana semakin kecil ukuran partikel, semakin rendah waktu vulkanisasi dan semakin tinggi laju vulkanisasi.

Keywords: curing characteristics, natural rubber, rubber mixing process

1. Introduction

Curing characteristic is a method used to observe the rate of rubber vulcanization reaction. It also can be used as a consideration basis for design of specimen and even rubber goods. A number of methods have been used to observe the rate of rubber vulcanization reaction. For example, Bideau *et al.* [1] employed a short-wave infrared irradiation, Jaunich *et al.* [2] monitored the vulcanization reaction by using online ultrasonic, Salgueiro *et al.* [3] used SANS and Pazur *et al.* [4] used NMR. Even some utilized DSC to observe the vulcanization reaction including Chough *et al.* [5], Machado *et al.* [6], and Ding *et al.* [7]. Although a number of methods have been applied to observe the vulcanization reaction, rheometer is still used in industries and research centers, even in Universities as carried out by Cotten [8], Gerspacher *et al.* [9], Mahalling *et al.* [10], Choi [11], Choi *et al.* [12], and Wang *et al.* [13]. The torque curve (as a function of vulcanization reaction time) is often called rheograph for it can be used to observe the rate of vulcanization reaction. The curing characteristics can be determined by using this instrument. According to Fath, a curing characteristic can be attained by composing rubber formula and considering physical properties that are going to be achieved [14]. The composed rubber formula is based on the setting of vulcanization system and the use of reinforcing fillers in rubber. It also can be obtained by modifying the sequence of rubber mixing process [15-18]. Although the sequence of rubber mixing process has been studied, a method to add carbon blacks into natural rubber and how long the mastication takes has not been specifically described. For that reason, this research aims to study the effects of mastication time and sequence of rubber chemicals as well as the addition of reinforcing fillers and its relationship with curing characteristics of natural rubber.

2. Experiment

The natural rubber, rubber chemicals, and reinforcing filler as illustrated in Table 1 were masticated and milled at temperature of 60 °C by respecting a set of rubber mixing sequence as seen in Table 2. This rubber sample was then identified as sample A. The addition sequence of carbon black was based on a stage as stated in Table 5 so that there would be samples A1, A2, A3, and A4.

The natural rubber formula in Table 1 was also used in mixing process that respects the sequence and time allocated for each mixing sequence as shown in Table 3 and 4. The sample that respected mixing sequence in Table 3 was identified as B and C while that respected mixing sequence in Table 4 was identified as D.

Table 1. Natural Rubber Formula

Materials	phr
Ribbed smoke sheet (RSS-1)	100
ZnO	5
Stearic acid	2
Carbon Black N 330/660	50
Paraffinic oil	5
Tetra methyl quinone (TMQ)	2
Tert butyl benzothiazole sulfenamide (TBBS)	0.5
Sulfur	2.5

Table 2. The Mixing Sequence of Natural Rubber Compound of A

Materials	Time, min
RSS-1	5
ZnO	2
Stearic acid	2
TMQ	1
CB_1	2
CB_2 + oil	4
TBBS	1
Sulfur	1

Table 3. The Mixing Sequence of Natural Rubber Compounds of B and C

Materials	Time, min
RSS-1	1
Stearic acid	1
Sulfur	2
ZnO	-
CB_1	3
CB_2 + oil	7
TBBS	6
TMQ	6

Remarks:

CB_1 is carbon black added at the first and CB_2+oli is the second addition of carbon black along with oil

Table 4. The Mixing Sequence of Natural Rubber Compound of D

Materials	Time, min
RSS-1	3
CB_1	2
CB_2 + oil	5
ZnO	2
Stearic acid	2
TMQ	1
TBBS	1
Sulfur	1

Table 5. The Addition of Carbon black into Natural Rubber under the Rubber Mixing Process

Code	CB_1	CB_2+oil
1	10 phr	40 phr+oil
2	20 phr	30 phr+oil
3	30 phr	20 phr+oil
4	40 phr	10 phr+oil

The addition sequence of carbon blacks to rubber respects such a sequence in Table 5 so that there would be samples B1, B2, B3, and B4; C1, C2, C3, and C4, D1, D2, D3, and D4. The mixing sequence in sample C equaled that in sample B but it utilized carbon black type N 660 as its reinforcing filler. After the milling process, curing characteristics of the rubber compounds are then determined by using rheometer MDR 2000. All this examination was done at temperature of 150 °C except for A1 and D1. To exhibit their curing characteristics, sample A1 and D1 were carried out at temperatures of 140 °C, 150 °C, 160 °C, and 170 °C. B1 and C1 are milled at temperatures of 55 °C, 60 °C, 65 °C, and 70 °C and vulcanized at temperature of 150 °C.

3. Results and Discussion

The curing characteristics of milling and mixing processes in Tables 2, 3 and 4 are illustrated in Table 6 while those of A1 and D1 as a function of vulcanization temperature are shown in Table 7. Table 8 illustrates curing characteristics of B1 and C1 as a function of mixing temperature.

Table 6 shows a comparison of the curing characteristics of compound A, B, C, and D. The maximum torque average of compound D is greater than that of A, B, and C. Referring to the mixing sequence in the mixing process described in Table 4, compound D was mixed and milled with carbon black at the first and then followed by mixing of rubber chemicals into the rubber. According to Wang (1998) carbon black surface has chance to absorb more rubber molecules so that the formation of bound rubber increases. The carbon black surface is not stained by rubber chemicals yet.

Illustration as described on Table 6, a maximum torque of compound A is greater than that of B and maximum torque of compound B is greater than that of C. Referring to illustration shown in Tables 2 and 3, compound A is masticated for 5 min while compound B is masticated for 1 min. The total time required to mill compound A is for 16 min and to compound B for 20 min while the order of mixing carbon black and rubber chemicals in the rubber compound A is the same as that of B, these mixing are simultant. High mastication time

causes soft rubber compound as well as the high total milling time. In this case, the role is to lower the maximum torque is rubber milling time. In the case of rubber chemicals mixing into the rubber, the compound B directly added stearic acid (a kind of fatty acids) so that the compound B is smooth besides the addition of sulfur first and followed by the addition of TBBS. This causes vulcanization reaction of compound B is slow. In compound A, stearic acid and ZnO are added together, and along with the addition of sulfur and TBBS into the rubber. Stearic acid and ZnO are an activator, sulfur is vulcanizing agent and TBBS is accelerator of vulcanization reaction. Compound A has high reaction rate compared to that of B. As consequence, compound A has high maximum torque.

The maximum torque of compound B is higher than that of C (Table 6). The mastication time, total milling time and mixing process of carbon black and rubber chemicals of rubber compound B is equal to that of C. Different type of carbon black is used. The particle size of carbon black used in the compound B is smaller than that of C. Small particle size of carbon black results a large surface area and the other way. The large surface area of carbon black is able to absorb more rubber backbones on the surface. For that reason, bound rubber becomes great so that maximum torque is high.

Table 6 also illustrates the influence of the mixing method of carbon black in rubber compounds A, B, C, and D. Maximum torque down with more and more carbon black mixed early in the milling process. The mixing of more carbon black in the beginning of milling process aims to utilize high rubber shearing force. Shearing force leads to high carbon black aggregates or agglomerates break into small particles. Small particle size causes the particles more easily dispersed in rubber. Thus the rubber molecules become more absorbed on the carbon black surface. Of course here is expected to be a higher maximum torque with more carbon black in the mix at the beginning of the process pengggilingan. However the data in Table 6 shows a decrease in maximum torque. This fact shows that the opposite order to the mixing method of carbon black in rubber more at the beginning of the milling process.

To resolve the above contradictions, another method is needed to overcome it. Choi (2004 and 2005) proposed curing time and curing rate. This method can be used to explain the curing characteristics of rubber clearly. Curing time and curing rate is calculated using the following equation:

$$\text{Curing rate} = \frac{(\text{Maximum Torque} - \text{Minimum Torque})}{(\text{Optimum curing} - \text{Scorch time})} \quad (1)$$

$$\text{Curing time} = (\text{Optimum curing} - \text{scorch time}) \quad (2)$$

Table 6. The Curing Characteristics of A, B, C and D at Temperature of 150 °C

Characteristics	Method	Rubber Mixing Process of Compounds															
		A				B				C				D			
		A1	A2	A3	A4	B1	B2	B3	B4	C1	C2	C3	C4	D1	D2	D3	D4
Maximum Torque, kg-cm		16.65	16.14	15.91	13.93	15.79	15.46	14.9	12.6	11.48	10.7	11.08	11.12	15.51	16.85	14.63	15.99
Minimum Torque, kg-cm		1.64	1.68	1.50	1.25	1.53	1.42	1.54	1.14	0.90	0.75	0.91	0.89	1.55	1.76	1.47	1.68
Max torque-min torque, kg-cm	ISO 6502-99	15.01	14.46	14.41	12.68	14.26	14.04	13.36	11.46	10.58	9.95	10.17	10.23	13.96	15.09	14.16	14.31
Optimum Curing (t90), min		11.57	11.02	11.05	11.16	10.31	10.23	10.51	10.18	10.25	10.15	10.11	10.13	10.23	11.09	10.24	10.39
Scorch time (ts2), min		2.19	2.25	2.29	2.33	2.14	2.13	2.18	2.3	3.12	3.06	3.07	3.09	2.18	2.15	2.18	2.27

Table 7. The Curing Characteristics of A1 and D1 under the Vulcanization Temperature of Compounds

Characteristics	Method	Temperature of Compounds							
		140 °C		150 °C		160 °C		170 °C	
		A1	D1	A1	D1	A1	D1	A1	D1
Maximum Torque, kg-cm		15.08	13.33	16.65	15.51	14.55	12.42	13.91	12.02
Minimum Torque, kg-cm		1.58	1.59	1.64	1.55	1.53	1.41	1.44	1.37
Max torque-min torque, kg-cm	ISO 6502-99	13.5	11.74	15.01	13.96	13.02	11.01	12.47	10.65
Optimum Curing (t90), min		20.12	25	11.57	10.23	5.29	6.28	2.56	3.26
Scorch time (ts2), min		3.41	4.04	2.19	2.18	1.09	1.17	0.43	0.48

Table 8. The Curing Characteristics of B1 and C1 under the Mixing Temperature of Compounds

Characteristics	Method	Temperature of Compounds							
		55 °C		60 °C		65 °C		70 °C	
		B1	C1	B1	C1	B1	C1	B1	C1
Maximum Torque, kg-cm		15.79	11.48	16.86	11.52	14.09	11.18	12.97	10.70
Minimum Torque, kg-cm		1.53	0.90	1.90	0.93	1.58	0.79	1.12	0.59
Max torque-min torque, kg-cm	ISO 6502-99	14.26	10.58	14.96	10.59	12.51	10.39	11.85	10.11
Optimum Curing (t90), min		10.31	10.25	11.35	11.00	10.4	9.56	12.08	12.46
Scorch time (ts2), min		2.14	3.12	2.16	3.06	2.28	3.07	2.09	2.58

From the equations (10) and (2), the rubber mixing process is then connected with the curing time and curing rate in the form of Fig. This Figure is used to explain not only the mixing method of carbon black more in the beginning of the process but also the mixing sequence of carbon black and rubber chemicals in the rubber.

Figure 1 indicates the decrease of curing time as well as the increase of curing rate from compound A1 to A4 generally. These tendencies occur as a result of the rubber milling process. The addition of more carbon blacks in the early rubber milling process causes its aggregates to fracture into smaller particles. The carbon black is easy to disperse into the rubber so that the contact surface between carbon black particles and rubber molecules get larger, leading it to function as a catalyst in vulcanization reaction [19].

Figure 2 shows the decrease of both curing time and curing rate in compound B1 to B4. Such a tendency also occurs in Figure 3 for compound C1 to C4 in which curing time of sample B was higher than that of

compound C. Similarly, curing rate of compound B is higher than that of C. Furthermore, curing time of compound A is higher than that of B while curing rate of compound A is lower than that of B. This means that vulcanization reaction of compound B is faster than that of A. On the other hand, Table 2 and 3 present the difference in addition sequences of TBBS and sulfur. In compound A, both TBBS and sulfur are added in the end of milling process while in compound B, sulfur is added first and then TBBS. In this stage, compound B points to a better sulfur dispersion in rubber than that of A, leading sulfur in compound B to serve as a better reactant or vulcanizing agent.

Both curing time and curing rate of compound C illustrated in Figure 3 are lower than that of B stated in Figure 2. The different type of added carbon black leads to different particle sizes in which particle size of carbon black in compound B is much smaller than that of C. The smaller particles cause carbon black to disperse easily into the rubber since the small particle size of carbon black results in the large surface area. Consequently, the contact area among rubber molecules

and carbon black surface get larger. In this case, carbon black can function as a catalyst in vulcanization reaction [19].

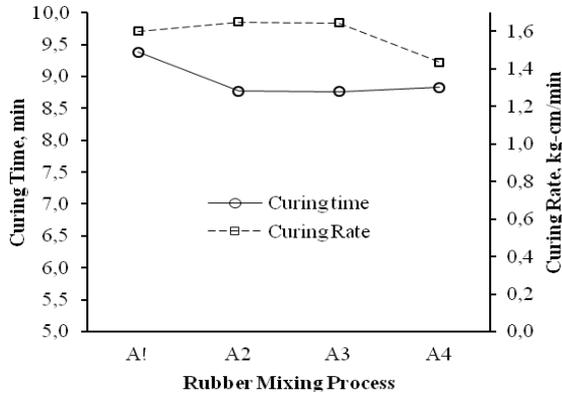


Figure 1. The Curing time and Curing Rate of A under the Rubber Mixing Process Effect at the Vulcanization Temperature of 150 °C

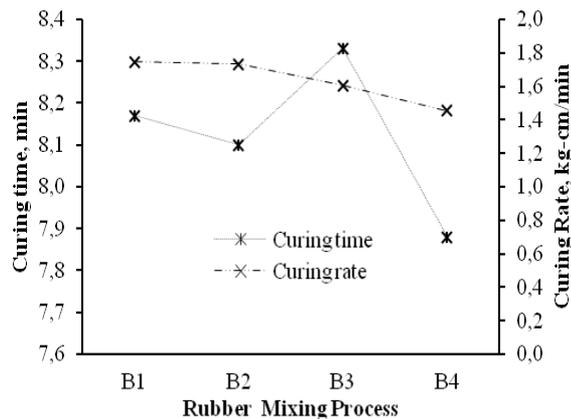


Figure 2. The Curing Rate of and Curing Rate of B under the Rubber Mixing Process Effect at the Vulcanization Temperature of 150 °C

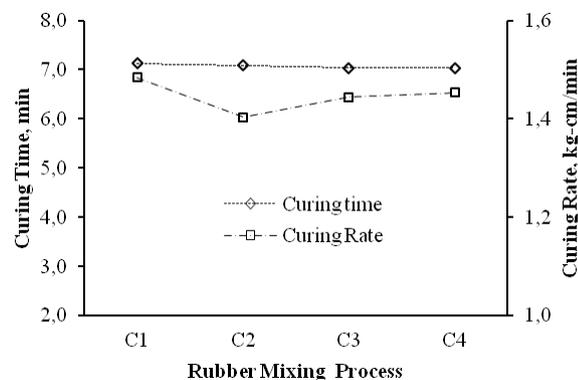


Figure 3. The Curing Rate of and Curing Rate of C under the Rubber Mixing Process Effect at the Vulcanization Temperature of 150 °C

Figure 4 states the decrease of both curing time and curing rate in compound D1 to D4. When compared to compounds A, B, and C, the compound D obviously demonstrates a high curing rate. As a consequence, vulcanization reaction rate of this compound is much faster than that of compounds A, B, and C. Table 4 indicates that the addition sequence of carbon black to rubber does not occur simultaneously with the addition of rubber chemicals. The carbon black is added at the first and then followed by the addition of rubber chemicals into the rubber. The better dispersion of carbon black is caused by high shearing force of rubber and its uncontaminated surface by rubber chemicals. In such a case, a better interaction between carbon black and rubber molecules occurs [20-24], leading carbon black to serve as a catalyst in vulcanization reaction.

Figure 5 shows the decrease of curing time as well as the increase of curing rate in compounds A1 and D1 at vulcanization temperatures of 140 °C, 150 °C, 160 °C, and 170 °C. These occurrences cannot be separated from vulcanization temperature in which high vulcanization temperature causes fast vulcanization reaction rate. Consequently, it leads curing time to decrease and curing rate to increase.

Figure 5 also shows that the curing time of compound A1 is the same as that of D1 but curing rate A1 is greater than that of D1. Referring to the explanation of Table 6, maximum torque D is greater than the maximum torque A so that bound rubber D is greater than that of A. Analogous to the description in Table 6, it can be concluded that the high bound rubber D causes curing rate low and on the contrary if low bound rubber results high curing rate.

Figure 6 illustrates the increase of curing time as well as the decrease of curing rate on compound B1 and C1 (from 140–170 °C). In these cases, of course, reaction

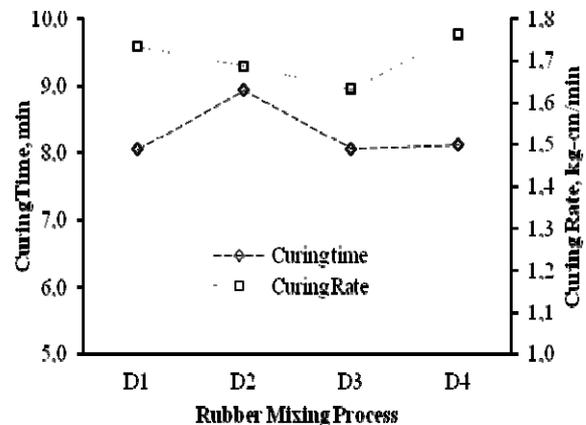


Figure 4. The Curing Rate of and Curing Rate of D under the Rubber Mixing Process Effect at the Vulcanization Temperature of 150 °C

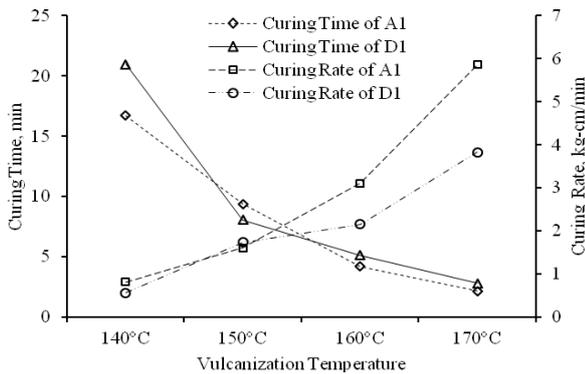


Figure 5. The Curing Time and Curing Rate of A1 and D1 under the Vulcanization Temperature Effect

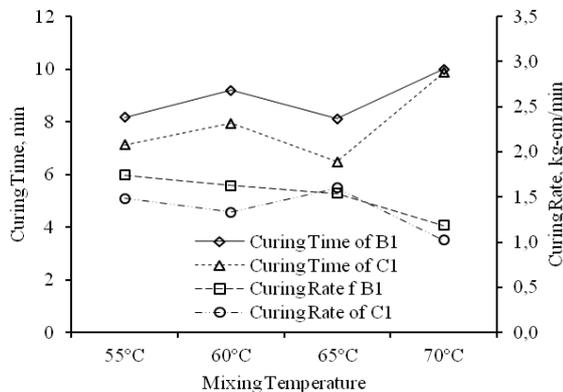


Figure 6. The Curing Time and Curing Rate of B1 and C1 under the Mixing Temperature Effect

rate of compound B1 and C1 decline with the increase of mixing temperature. As temperature increases, the rubber viscosity and shearing force also decreases so that carbon black is well-dispersed into the rubber but it will be dispersed again in form of larger particles. The surface area of carbon black aggregates is much narrower than that of its particle form so that the carbon black cannot serve as a catalyst. Such a case (as indicated in compound B) also takes place in compound C under the effect of rubber mixing temperature.

Figure 6 also informs that the curing rate B1 is higher than that of C1. This is due to the size of the carbon black particles in the compound B1 is smaller than that of C1. Small particle size causes carbon black more easily dispersed into the rubber so that it can better serve as a catalyst in the vulcanization reaction of compound B1 compared to that of C1.

4. Conclusions

Curing characteristic is an indicator of rubber vulcanization reaction rate. The curing results exhibit

physical properties of vulcanized rubber. The more carbon black added in the early milling process cause the low curing time and the high curing rate. Meanwhile, particle size of carbon black has an effect on curing time and curing rate. The small particle size results the low curing time and the high curing rate. The addition of carbon black in the early rubber mixing process before that of rubber chemicals addition results in better curing time and curing rate than the simultaneous addition of carbon black into the rubber. Furthermore, the mixing temperature also gives an impact on the curing characteristic in which the high mixing temperature causes the low curing time and curing rate.

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References

- [1] P.L. Bideau, J.P. Plateau, P. Dutournie, P. Glouance. *Intl. J. Thermal Sci.* 48 (2000) 573.
- [2] M. Jaunich, W. Stark, B. Hoster, *Polymer Testing*. 28 (2009) 84.
- [3] W. Salgueiro, A. Samoza, I.L. Torriani, A.J. Marzocca, *J. Polym. Sci. Part B: Polym Phys.* 45 (2007) 2966.
- [4] R.J. Pazur, F.J. Walker, M.I. Plymout, *Kautschuk Gummi Kunststoffe*. Jan/Feb (2011)16.
- [5] S.H. Chough, D-H. Chang, *J. Appl. Polym. Sci.* 61 (1996) 449.
- [6] M.A. Manchado, M. Arroyo, J. Herrero, J. Biagiotti, *J. Appl. Polym. Sci.* 89 (2003) 1.
- [7] R. Ding, A.I. Leonov, *J. Appl. Polym. Sci.* 61 (1996) 455.
- [8] G.R. Cotton, *Rubber Chem. Technol.* 45 (1972) 124.
- [9] M. Gerspacher, L. Niliel, H.Y. Yang, C.P. O'Farrel, G.A. Schwartz, Paper Presented at a Meeting of the Rubber Division, American Chemical Society, USA, 2001.
- [10] R.N. Mahaling, S. Kumat, T. Rath, C.K. Das, *J. Elas. Plast.* 39 (2007) 253.
- [11] S.S. Choi, *J. Appl. Polym. Sci.* 93 (2004) 1001.
- [12] S.S. Choi, K.J. Hwang, B.T. Kim, *J. Appl. Polym. Sci.* 98 (2005) 2282.
- [13] P.Y. Wang, H.L. Qian, H.P. Yu, J. Chen, *J. Appl. Polym. Sci.* 88 (2003) 680.
- [14] M.A. Fath, *Rubber World* 208 (1993) 15.
- [15] M.J. Wang, In *Proceedings of International Rubber Conference (IRC)*, France, 2006.

- [16] M.J. Wang, Rubber Chem. Technol. 71 (1998) 520.
- [17] M.J. Wang, Paper Presented at a Meeting of the Rubber Division, American Chemical Society, USA, 1998.
- [18] F.M. Dannenberg, Rubber Chem. Technol. 59 (1986) 512.
- [19] N. Tricas, E.V. Escalas, S. Barros, Afinidad. 59 (2002) 337.
- [20] S. Wolff, M.J. Wang, E.H. Tan, Rubber Chem. Technol. 66 (1993) 163.
- [21] B. Meissner, Rubber Chem. Technol. 68 (1995) 297.
- [22] P.K. Pal, A.K. Bhowmick, S.K. De, Rubber Chem. Technol. 55 (1982) 23.
- [23] J.B. Horn, B.B. Boonstra, In: C.M. Blow, C. Hephurn, Rubber Technology and Manufacture. 2nd, Butterworth Scientific, London, 1982 p.202 and p.269.
- [24] S. Qian, J. Huang, W. Guo, Chifei Wu, J. Macromol Sci. Part B: Physics. 46 (2007) 453.