IOSR Journal of Polymer and Textile Engineering (IOSR-JPTE)
e-ISSN: 2348-019X, p-ISSN: 2348-0181, Volume 3, Issue 5 (Sep. - Oct. 2016), PP 01-07
www.iosrjournals.org

Effects of Silanized Fillers and Accelerators on the Cure and Chemical Characteristics of NR/SBR/EPDM Blend

Soh Tiak Chuan[1]
[1](Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia, 76100, Durian Tunggal, Melaka, Malaysia)

Abstract: *Effects of silanized fillers on the hybrid silica / calcined clay and accelerators synergism with mercaptobenzothiazole disulfide (MBTS) / Zn-2-mercaptobenzothiazole (ZMBT) / diphenyl guanidine (DPG) on the cure and chemical characteristics of an industrial natural rubber (NR) / styrene butadiene rubber (SBR) / ethylene propylene diene terpolymer (EPDM) rubber blend were investigated. 20 samples, with 5 levels of fillers (0.00 phr, 3.78 phr, 11.44 phr, 15.61 phr and 18.29 phr) and 4 levels of accelerators (0.04 phr, 1.11 phr, 2.30 phr and 3.50 phr)were subjected for the characterizations of rheometry cure characteristics, bound rubber content (BRC) and fourier transform infrared (FTIR). The cure rate activation effect increases as a direct function when increasing in the loadings of accelerators. However due to the absorptions of accelerators and soluble zinc from the silanol side groups of fillers, the cure rate of vulcanizates decreases when increasing in the loadings of fillers. Rubber crosslink density is enhanced when the loadings of both accelerators and fillers are increased. In terms of BRC, it increases onward from the fillers loading of 11.44 phr attributed to the improvement of rubber-filler interaction. FTIR results support well the findings of cure and rubber-filler interaction via the insights of chemical bonding.*

Keywords: *Bound rubber content, cure characteristics, fourier transform infrared, rubber accelerators, rubber fillers.*

I. Introduction

Fillers are essentially in imparting satisfactory rubber properties, processing behaviour and reduction of compound cost. Silica can impart significant improvement on rubber mechanical properties as revealed in many researches [1, 2, 3]. When silica is hybridized with clay, the reinforcing capability of rubber is better than the individual adding of filler supported by numerous researchers [4,5] attributable to the multiphase-filler system that retains the advantages of all fillers which provide synergism on rubber reinforcement. On the other hand, rubber cure accelerators are used to accelerate the cure rate of sulfur-cured system in rubber vulcanization. Cure synergism for the combination of accelerators mercaptobenzothiazole disulfide (MBTS) / Zn-2-mercaptobenzothiazole (ZMBT) / diphenyl guanidine (DPG) instigates better mechanical properties for rubber vulcanizates which can benefit industrial application [6]. However, researches with regard to rheometry, bound rubber content (BRC) and chemical bonding fourier transform infrared (FTIR) on hybrid fillers in the present of accelerators have not been investigated thoroughly.

Present study focused on the cure and chemical characteristics by referring to an industrial high degradation resistance natural rubber (NR) / styrene butadiene rubber (SBR) / ethylene propylene diene terpolymer (EPDM) rubber blend used for the production of rubber molded mat. NR serves as a main rubber whereas EPDM is added due to its excellent degradation resistance [7]. The results allow better insights on these aspects in correlating with the enhancement of mechanical properties for this specific industrial rubber compound.

II. Experimental

2.1 Materials

Natural rubber (NR) (L-grade) was supplied by Hockson Rubber Trading, ethylene propylene diene terpolymer (EPDM) (Nordel P4520) with Mooney viscosity 20 was supplied by Dow Chemical, styrene butadiene rubber (SBR) (Intol 1502) with Mooney viscosity 52 was supplied by Polimeri Europa UK Ltd. Silane coupling agent, 3-triethoxysilyl propyltetrasulfide (TESPT) was supplied by Innova Chemical Co. Ltd. Precipitated silica with a surface area of 161-190 m^2/g was supplied by Euro Chemo Sdn. Bhd. Calcined clay with a surface area of 12-16 m^2/g was supplied by Tangshan Madison Kaolin Co. Ltd. Calcium carbonate ($CaCO_3$) with an average particle size of 7.6-8.5 µm and coated with stearic acid was supplied by Zantat Sdn. Bhd. Accelerators mercaptobenzothiazole disulfide (MBTS) with purity > 96% was supplied by Luxchem, Zn-2-mercaptobenzothiazole (ZMBT) with Zn content of 18-20 % and diphenyl guanidine (DPG) with purity > 96 % were supplied by Lanxess. Other rubber ingredients of zinc oxide (ZnO), stearic acid, polyethylene glycol, paraffinic oil, metal soap, homogenizing resin and sulfur were the grades customarily used in rubber industries.

2.2 Formulations and Mixing

20 samples (S1-S20) were prepared by using a two wings tangential 110 liter internal mixer (X(S)N-110/30) from Dalian ChengXin Rubber & Plastics Machinery Co. Ltd., China with a friction ratio of 1.22. The formulations are depicted in Table 1. The basis of formulation was referring to an industrial compound for the production of high degradation resistance rubber molded mat added with 20 phr $CaCO_3$. The samples were added with different loadings of hybrid fillers (silica / calcined clay) and accelerators (DPG / ZMBT / MBTS). The ratios of silica / calcined clay and DPG / ZMBT / MBTS were fixed at 1:1.86 and 1:1:20 respectively. Five levels of loadings for hybrid fillers are 0.00 phr, 3.78 phr, 11.44 phr, 15.61 phr and 18.29 phr. In terms of accelerators, four levels were selected i.e. 0.04 phr, 1.11 phr, 2.30 phr and 3.50 phr.

Table 1 Formulations of S1-S20

Ingredient	S1 (phr[a])	S2 (phr[a])	S3 (phr[a])	S4 (phr[a])	S5 (phr[a])	S6 (phr[a])	S7 (phr[a])	S8 (phr[a])	S9 (phr[a])	S10 (phr[a])
NR	66.22	66.22	66.22	66.22	66.22	66.22	66.22	66.22	66.22	66.22
SBR	13.91	13.91	13.91	13.91	13.91	13.91	13.91	13.91	13.91	13.91
EPDM	19.87	19.87	19.87	19.87	19.87	19.87	19.87	19.87	19.87	19.87
$CaCO_3$	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
Silica	-	1.32	4.00	5.46	6.40	-	1.32	4.00	5.46	6.40
Calcined clay	-	2.46	7.44	10.15	11.89	-	2.46	7.44	10.15	11.89
ZnO	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18
Stearic acid	4.77	4.77	4.77	4.77	4.77	4.77	4.77	4.77	4.77	4.77
DPG	0.002	0.002	0.002	0.002	0.002	0.05	0.05	0.05	0.05	0.05
ZMBT	0.002	0.002	0.002	0.002	0.002	0.05	0.05	0.05	0.05	0.05
MBTS	0.036	0.036	0.036	0.036	0.036	1.01	1.01	1.01	1.01	1.01
PEG	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48
Paraffinic oil	-	0.76	2.29	3.12	3.66	-	0.76	2.29	3.12	3.66
Resin	-	0.38	1.14	1.56	1.83	-	0.38	1.14	1.56	1.83
Metal soap	-	0.47	1.43	1.95	2.29	-	0.47	1.43	1.95	2.29
TESPT	-	0.76	2.29	3.12	3.66	-	0.76	2.29	3.12	3.66
Sulfur	1.59	1.59	1.59	1.59	1.59	1.59	1.59	1.59	1.59	1.59
Total	130.06	136.21	148.65	155.42	159.79	131.13	137.28	149.72	156.49	160.86

Ingredient	S11 (phr[a])	S12 (phr[a])	S13 (phr[a])	S14 (phr[a])	S15 (phr[a])	S16 (phr[a])	S17 (phr[a])	S18 (phr[a])	S19 (phr[a])	S20 (phr[a])
NR	66.22	66.22	66.22	66.22	66.22	66.22	66.22	66.22	66.22	66.22
SBR	13.91	13.91	13.91	13.91	13.91	13.91	13.91	13.91	13.91	13.91
EPDM	19.87	19.87	19.87	19.87	19.87	19.87	19.87	19.87	19.87	19.87
$CaCO_3$	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
Silica	-	1.32	4.00	5.46	6.40	-	1.32	4.00	5.46	6.40
Calcined clay	-	2.46	7.44	10.15	11.89	-	2.46	7.44	10.15	11.89
ZnO	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18
Stearic acid	4.77	4.77	4.77	4.77	4.77	4.77	4.77	4.77	4.77	4.77
DPG	0.10	0.10	0.10	0.10	0.10	0.16	0.16	0.16	0.16	0.16
ZMBT	0.10	0.10	0.10	0.10	0.10	0.16	0.16	0.16	0.16	0.16
MBTS	2.10	2.10	2.10	2.10	2.10	3.18	3.18	3.18	3.18	3.18
PEG	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48
Paraffinic oil	-	0.76	2.29	3.12	3.66	-	0.76	2.29	3.12	3.66
Resin	-	0.38	1.14	1.56	1.83	-	0.38	1.14	1.56	1.83
Metal soap	-	0.47	1.43	1.95	2.29	-	0.47	1.43	1.95	2.29
TESPT	-	0.76	2.29	3.12	3.66	-	0.76	2.29	3.12	3.66
Sulfur	1.59	1.59	1.59	1.59	1.59	1.59	1.59	1.59	1.59	1.59
Total	132.32	138.47	150.91	157.68	162.05	133.52	139.67	152.11	158.88	163.25

[a] Part per hundred rubber

2.3 Characterizations of Samples

Cure characteristics were determined by using an oscillating rotorless rheometer (UR2010) from U-CAN Dynatex Inc., Taiwan. The upper and lower dies in compliance with ASTM D5289 are set at temperature 165 °C, pressure 4.5 kg/cm^2 and for a running time of 240 sec. The data of cure characteristics for scorch time (T_2 in unit second), 90 % cure time (T_{90} in unit second), cure rate index (CRI in unit minute^{-1}) and torque difference (Δ torque in unit dNm) were recorded for every sample. CRI, which is a measure of cure reaction [8] is given as:

$$\mathrm{CRI}\ (\mathrm{min}^{-1}) = \frac{100}{T_{90} - T_2} \qquad (1)$$

Δ torque, which represents the crosslink density [8] is given as:

$$\Delta\ \text{torque} = \text{MH} - \text{ML} \qquad (2)$$

where MH and ML are maximum and minimum torque, respectively.

Test of bound rubber content (BRC) for the analysis of rubber-filler interaction for an uncured rubber was only focused on the samples S16-S20 which added with 3.50 phr of accelerators but varying across 5 levels of fillers loadings. 3 g of compound was cut into several small pieces and immersed inside 150 ml toluene (density of 0.865 g/ml and boiling point of 110 ^{0}C) for 72 hours at 25 ^{0}C. After this time elapsed, the solvent was removed and the remnant of swollen gel was put into 100 ml acetone for 24 hours to remove the residue toluene. The sample was then dried at room temperature for 24 hours inside a dehumidifier. Next, oven drying at 85 ^{0}C for 24 hours was carried out until obtaining a dried sample. The dried sample was subsequently subjected for an extra 24 hours drying inside the dehumidifier again before it was accurately re-weighed. The BRC was calculated by using Equation 3 [9]:

$$R_B = \frac{W_{fg} - W_t\left[\frac{m_f}{(m_f + m_r)}\right]}{W_t\left[\frac{m_r}{(m_f + m_r)}\right]} \times 100\ \% \qquad (3)$$

where W_{fg} is the weight of filler and gel, W_t is the weight of predetermined 3 g sample, m_f is the fraction of filler in the compound and m_r is the fraction of rubber in the compound.

Fourier-transform infrared (FTIR) spectroscopy was carried out by using a machine of model Spectrometer 6700. Attenuated total reflectance (ATR) through attenuated radiation of IR beam by using a diamond ATR crystal was used to analyze the spectra of the samples in the range of 400–4000 cm^{-1}. The center part for the cured disc of rheometry at thickness 0.2 mm as Fig. 1 was used for FTIR-ATR test.

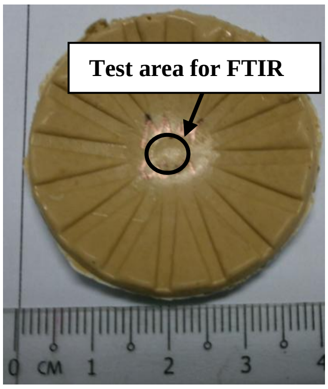


Fig. 1 Centre test area for FTIR derived from the test disc of rheometry

III. Results and Discussion

3.1 Cure Characteristics and Bound Rubber Content (BRC)

Table 1 exhibits the average results of rheometry cure characteristics and BRC from 3 repetitions of test for each sample. Values of T_2 decrease sharply when the contents of accelerators are increased from 0.04 phr until 3.50 phr. When comparing across the compounds at 0 fillers content, increase in accelerators loadings from 0.04 phr to 3.50 phr involves a remarkable 39.2 % reduction in T_2. As long T_2 implies slow onset of cure, the accelerators level at 0.04 phr exhibits extraordinary long T_2 that limits its ability to initiate sulfuric crosslinking. In terms of the factor of fillers, decreasing trends of T_2 are observed across all levels of accelerators (0.04-3.50 phr) when the amounts of fillers are increased especially starting from 11.44 phr until 18.29 phr. The declining trend may be ascribed to greater thermal history of shear mixing when increasing the loadings of fillers that lead to enhanced compound viscosity. Besides, the silane coupling agent, TESPT can act as sulfur donor to accelerate the onset of cure. It is in-line with Sengloyluan and co-workers [10] who noticed shorter T_2 for the silica-filled compound added with TESPT.

The compounds of highest loading of accelerators at 3.50 phr manifest lowest cure times T_{90}. On the contrary, the compounds of lowest loading of accelerators at 0.04 phr manifest excessively long cure times i.e. at the range of 283.00-285.33 sec., which such long cure time are impractical industrially. For the factor of fillers, interestingly, slight longer values of T_{90} are observed when increasing in the loadings of fillers which are contradictory with T_2. For rubber compounds, adding of silica and calcined clay may absorb the accelerators and soluble Zn through their silanol side groups. Numerous researchers [3, 5, 11] have observed the increasing trends of cure times for the silica-reinforced rubber compounds. With respects to CRI values, the levels of accelerators serve as a direct function over CRI. Higher cure rate supports better cure activation effect for the compounds of sufficient accelerators. In terms of fillers, CRI values are lower for the compounds added with higher loadings of fillers attributed to their longer T_{90} and shorter T_2.

Since Δtorque reflects the amount of sulfur crosslinks formed at a given temperature, significant reductions in Δtorque for the compounds added with lower loadings of accelerators are observed. At extremely low 0.04 phr accelerators, values of Δtorque are below 5 dNm for all compounds and increase proportionally until 3.50 phr. In this context, higher loadings of accelerators increase the degree of crosslinking. For the factor of fillers, it enhances the Δtorque of compounds. It is deduced that silane coupling agent yields extra crosslinks with rubber matrix which enhances further the crosslink density of rubber. The result corresponds well with other researchers [12, 13, 14] who revealed increased trends of crosslink density resulting from enhanced silane-filler linkages in the presence of silane coupling agent in rubber compounds.

Table 2 Cure characteristics and BRC of S1-S20

Accelerators loading	Sample	T_2 (sec.)	T_{90} (sec.)	CRI (min^{-1})	Δ torque (dNm)	BRC (%)
0.04 phr	S1(0.00[a])	165.00	283.00	50.85	4.02	-
	S2 (3.78[a])	166.00	283.33	51.14	4.13	-
	S3 (11.44[a])	164.67	284.67	50.00	4.35	-
	S4 (15.61[a])	155.33	284.33	46.51	4.45	-
	S5 (18.29[a])	145.33	285.33	42.26	4.92	-
1.11 phr	S6 (0.00[a])	125.00	241.67	51.43	11.23	-
	S7 (3.78[a])	126.33	248.00	49.33	11.61	-
	S8 (11.44[a])	126.33	253.33	47.25	11.53	-
	S9 (15.61[a])	118.00	254.67	43.91	12.18	-
	S10 (18.29[a])	115.00	255.67	42.66	12.90	-
2.30 phr	S11 (0.00[a])	116.33	175.00	102.28	15.16	-
	S12 (3.78[a])	116.00	174.67	102.28	15.61	-
	S13 (11.44[a])	114.67	181.67	89.55	16.16	-
	S14 (15.61[a])	113.67	187.00	81.86	16.88	-
	S15 (18.29[a])	113.33	192.67	75.64	17.12	-
3.50 phr	S16 (0.00[a])	100.33	152.00	116.20	17.04	undetected BRC
	S17 (3.78[a])	99.67	154.67	109.11	17.66	undetected BRC
	S18 (11.44[a])	100.67	161.67	93.38	18.35	34.614
	S19 (15.61[a])	99.33	163.00	94.25	18.32	38.250
	S20 (18.29[a])	99.33	174.67	79.67	18.66	39.046

[a] Loading of fillers (silica / calcined clay) in phr

Results of BRC for S18, S19 and S20 are 34.614 %, 38.250 % and 39.046 % respectively. The silica-filled compounds added with silane coupling agent form the chemical bonds between rubber and silica which enhance the BRC than the compounds without added with silane [10, 15]. S20 added with highest level of fillers at 18.29 phr appears to be highest in BRC among the samples supports highest silanization reaction in forming highest amount of silanized fillers which subsequently interacts with rubber matrix. The silanization reaction is exhibited in Fig. 2.

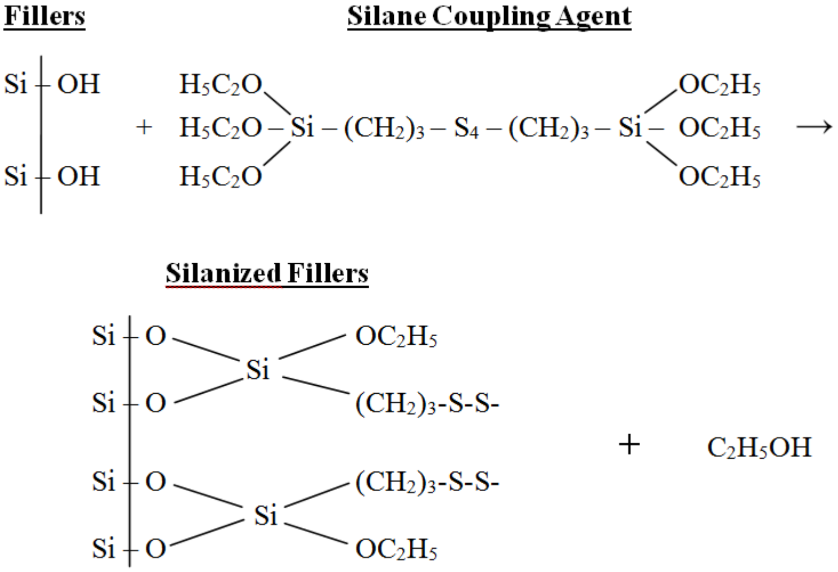
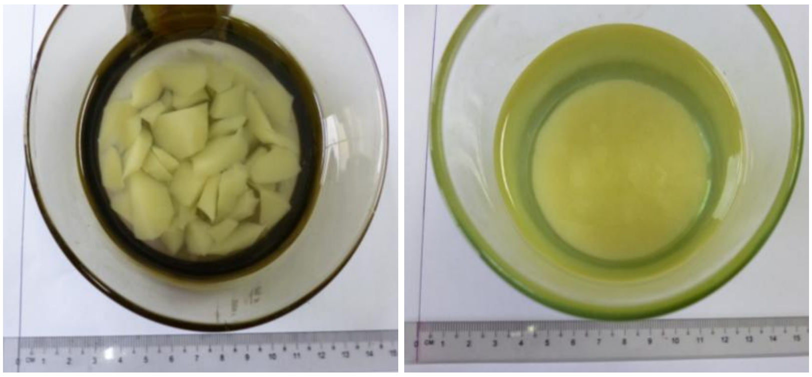


Fig. 2 Silanization reaction of fillers and silane coupling agent

Nevertheless, for S16 and S17, they were fully diluted in toluene after 72 hours of solvent immersion and the remnants of filler and gel were unobtainable. These compounds at low levels of silanized fillers are rather poor in rubber-filler interaction. As BRC involves the extraction of free rubber portion from an unvulcanized compound leaving the polymer portion remains bounded to the filler [2, 9], weak rubber-filler interactions of S16 and S17 make the rubber particles fully separated from the fillers phase under toluene swelling effect. Fig. 3 illustrates a sample of swollen compound which allows extraction of BRC and a sample of fully diluted compound which prevents attaining of BRC.



(a) (b)

Fig. 3 Swollen compound (a) and fully diluted compound (b) after toluene immersion for the test of BRC

3.2 Fourier Transform Infrared (FTIR)

Fig. 4 represents the FTIR spectra of 500-4000 cm^{-1} for the samples S3, S8, S13, S16, S18 and S20. Samples S3, S8, S13 and S18 represent the equal level of fillers at 11.44 phr but different levels of accelerators at 0.04 phr, 1.11 phr, 2.30 phr and 3.50 phr respectively. They were selected to analyze on the accelerators factor. Analysis on the fillers factor involves S16, S18 and S20 at the equal level of accelerators at 3.5 phr but different levels of fillers at 0 phr, 11.44 phr and 18.29 phr respectively.

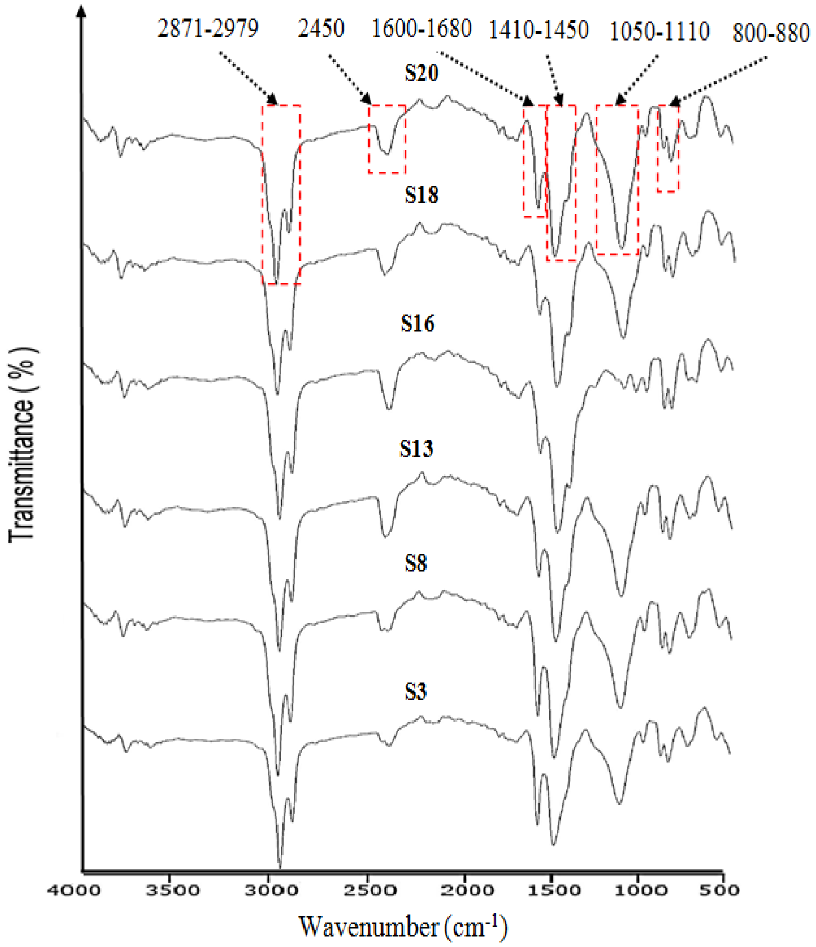


Fig. 4 FTIR spectra for S3, S8, S13, S16, S18 and S20

All spectra exhibit similar peak intensities of 800-880 and 1410-1450 cm^{-1} for the $CaCO_3$ filled vulcanizates [16] ascribed to equal 20 phr loadings of this material as well as parallel peak at 2871-2979 cm^{-1} representing the involvement of $–CH_3$ and $–CH_2–$ [16] from the polyisoprene bending of NR which served as the main rubber. Prominent intensity at peak 1600-1680 cm^{-1} is seen for S3 which added with lowest accelerators at 0.04 phr and reduces proportionally when increasing in accelerators levels. It supports higher unsaturation of rubber backbones and more C=C stretching which represents low crosslink density as evidenced via previous cure characteristics analysis at low accelerators levels particularly for S3. It is in agreement with the observations of Gac et al. [17] at the similar distinct peaks arising from the unsaturation of C=C rubber chains. Aromatic hydrocarbons produce the band at 2450 cm^{-1} [18]. A gradual increase of peak at 2450 cm^{-1} from S3 until S16 is in agreement with higher loadings of accelerators from 0.04 phr until 3.50 phr as the chemical natures of DPG, ZMBT and MBTS are bounded to aromatic benzene chemical linkages. The results are complementing with increased trend of cure rate activation proportional to the increase of accelerators. Peak of 1050-1110 cm^{-1} relates to stretching vibration of Si-O-C [19, 20]. In this connection, a gradual increase at this peak from S16 until S20 is in accordance to Si-O-C stretching attributable to the chemical absorptions of bulk isoprene polymer on the silica surfaces. The results evidence appreciably enhanced silanization reaction was realized which has improved the rubber-filler interaction.

IV. Conclusion

Present research presented the effects of different levels of hybrid fillers and accelerators on the changes of cure characteristics, bound rubber content and fourier transform infrared of rubber vulcanizates referring to a basis formulation of rubber molded mat. Cure rate activation and crosslink density serve as the direct functions against the increase of accelerators loadings. Bound rubber content shows an apparent increase from 34.614 % to 39.046 % when the loadings of fillers are increased from 11.44 % until 18.29 % support enhanced silanization reaction with increased amounts of silanized fillers. Both observations of cure characteristics and bound rubber content correspond well with the results of infrared spectra analyzed through FTIR characterizations on chemical bonding.

References

[1]. S. Ray, Silica-filled polymer microcomposites, in S. Thomas, K. Joseph, S.K. Malhotra, K. Goda, and M.S. Sreekala, (Ed.) *Polymer Composites,* (Weinheim: Wiley-VCH, 2012) 545-574.

[2]. A. Mostafa, A. Abouel-Kasem, M.R. Bayoumi, and M.G. El-Sebaie, Rubber-filler interactions and its effect in rheological and mechanical properties of filled compounds, *Journal of Testing and Evaluation, 38(3),* 2014, 1-13.

[3]. S.Y. Yang, L. Liu, Z.X. Jia, W.W. Fu, D.M. Jia, and Y.F. Luo, Study on the structure-properties relationship of natural rubber/SiO_2 composites modified by a novel multi-functional rubber agent, *eXPRESS Polymer Letters*, *8(6),* 2014, 425–435.

[4]. H. Ismail, and M. Mathialagan, Comparative study on the effect of partial replacement of silica or calcium carbonate by bentonite on the properties of EPDM composites, *Polymer Testing, 31,* 2012, 199-208.

[5]. Q. Zhang, Q. Liu, Y. Zhang, H. Cheng, and Y. Lu, Silane-grafted silica-covered kaolinite as filler of styrene butadiene, *Applied Clay Science, 65,* 2012, 134-138.

[6]. Q.Ahsan, N. Mohamad, and T.C. Soh, Effects of accelerators on the cure characteristics and mechanical properties of natural rubber compounds, *International Journal of Automotive and Mechanical Engineering, 12,* 2015, 2954-2966.

[7]. S. Soundararajan, and K. Palanivelu, Studies on mechanical and electrical properties of poly carbonate-EPDM blends, *IOSR Journal of Polymer and Textile Engineering, 1(2),* 2014, 8-10.

[8]. M. Sabzekar, M.P. Chenar, S.M. Mortazayi, M. Kariminejad, S. Asadi, and G. Zohuri, Influence of process variables on chemical devulcanization of sulfur-cured natural rubber, *Polymer Degradation and Stability, 118,* 2015. 88-95.

[9]. S.S. Choi, and E. Ko, Novel test method to estimate bound rubber formation of silica-filled solution styrene-butadiene rubber compounds, *Polymer Testing, 40,* 2014, 170-177.

[10]. K. Sengloyluan, K. Sahakaro, W.K. Dierkes, and W.M. Noordermeer, Silica-reinforced tire tread compounds compatibilized by using epoxidized natural rubber, *European Polymer Journal, 51,* 2014, 69-79.

[11]. S.M. Hosseini, and M.R. Kashani, Vulcanization kinetics of nano-silica styrene butadiene rubber, *Polymer, 55,* 2014, 6426-6434.

[12]. S. Pattanawanidchai, S. Loykulnant, S. Pongdhorn, N. Maneevas, and C. Sirisinha, Development of eco-friendly coupling agent for precipitated silica filled natural rubber compounds, *Polymer testing, 34,* 2014, 58-63.

[13]. T. Theppradit, P. Prasassarakich, and S. Poompradub, Surface modification of silica particles and its effects on cure and mechanical properties of the natural rubber composites, *Materials Chemistry and Physics, 148,* 2014, 940-948.

[14]. X. Ge, M.C. Li, X.X. Li, and U.R. Cho, Effects of silane coupling agents on the properties of bentonite/nitrile butadiene rubber nanocomposites synthesized by a novel green method, *Applied Clay Science, 118,* 2015, 265–275.

[15]. S.S. Sarkawi, W.K. Dierkes, and W.M. Noordermeer, Elucidation of filler-to-filler and filler-to-rubber interactions in silica-reinforced natural rubber by TEM Network Visualization, *European Polymer Journal, 54,* 2014, 118-127.

[16]. A. Alkhaibari Abdulmuttalib Mohammed, and J. Wang, Properties of nano calcium carbonate reinforced polypropylene/POE nanocomposites, *IOSR Journal of Polymer and Textile Engineering, 3(3),* 2016, 1-10.

[17]. P.Y.L. Gac, M. Broudin, G. Roux, J. Verdu, P. Davies, and B. Fayolle, Role of strain induced crystallization and oxidative crosslinking in fracture properties of rubber, *Polymer, 55,* 2014, 2535-2542.

[18]. B. Stuart, *Infrared spectroscopy: Fundamentals and applications* (New Jersey: John Wiley & Sons, Ltd, 2004).

[19]. T. Xu, Z. Jia, Y. Luo, D. Jia, and Z. Peng, Interfacial interaction between the epoxidized natural rubber and silica in natural rubber/silica composites, *Applied Surface Science, 328,* 2015, 306–313.

[20]. F. Yan, X. Zhang, F. Liu, X. Li, and Z. Zhang, Adjusting the properties of silicone rubber filled with nanosilica by changing the surface organic groups of nanosilica, *Composites, 75,* 2015, 47-52.