Time Factor on Premature Cure and Bound Rubber Content of a Silanized NR/EPDM/SBR Blend

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Abstract The effects of premature cure and bound rubber content (BRC) of a 3-triethoxysilyl propyltetrasulfide (TESPT) silanized natural rubber (NR) / ethylene propylene terpolymer EPDM / styrene butadiene rubber (SBR) blend added with hybridized precipitated silica and calcined clay over 6 months of storage period were investigated. The significant correlations between the cure characteristics of scorch time (T2) and cure rate index (CRI) over 6 months of ambient storage period analyzed in monthly basis were determined by using statistical correlation r technique. Fourier-transform infrared (FTIR) was used to observe the possible changes of chemical bonding vibration throughout this storage period in supporting the findings of cure characteristics with regard to the trend of premature cure. Solvent extraction method was used to determine the BRC of the compound over the storage period. It is observed that the sulfide groups of TESPT do not show significant crosslink tendency with rubber matrix and thus without depicting the trend of premature cure throughout the ambient storage period. However, BRC of compound is increased by 75.01 % after one month of ambient storage and level off thereafter represent a marked increase of rubber-filler interaction within the first storage month.

Keywords Scorch Time, Cure Rate Index, Bound Rubber Content, Storage Period, Silanization

Introduction

Adding of silane coupling agent in rubber compounds can promote the rubber-filler interaction and mechanical properties of vulcanizates added with silica [1-3] and clay [4-6]. In silanization reactions, the one end of alkoxy groups of silane react with the hydroxyls of filler surface, whilst the other end of sulfide groups interact with the double bonds of rubber molecules forming strong chemical linkages [7,8]. Silica-filled compounds added with silane coupling agent form rubber-filler chemical bonds which increase their bound rubber content (BRC) [2,9]. Measurement of BRC is a practical way to evaluate the extent of rubber-filler interaction of rubber compound indicating the degree of adhesion of rubber matrix to filler surface which is important in rubber reinforcement [10,11]. Organosilane 3-triethoxysilyl propyltetrasulfide $[(C_2H_5O)_3Si-(CH_2)_3-S_4-(CH_2)_3-Si(C_2H_5O)_3]$ or TESPT is reportedly the common and successful organosilane used to modify silica in the sulfur-cured rubber compounds [6,12]. In actual application, TESPT reacts with rubber with or without elemental sulfur at high temperature especially at prolonged mixing time and high mixing temperature [13]. The high sulfur ratio of TESPT makes it a sulfur donor which imparts premature-cured reactions with rubber [14]. Premature cure of rubber compounds can render to processing difficulties in rubber industry. However, the changes of premature cure and BRC of TESPT-added rubber throughout long period storage have not been investigated. Thus, present study is carried out to analyze the changes in monthly basis on these respects against a total 6 months period of ambient storage for an industrial used silanized NR/EPDM/SBR blend added with hybridized precipitated silica and calcined clay.

Materials and Methods

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. 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. Other rubber ingredients of zinc oxide (ZnO), titanium dioxide, stearic acid, polyethylene glycol, phenolic antioxidant, paraffinic oil, metal soap, homogenizing resin, mercaptobenzothiazole disulfide (MBTS), diphenyl guanidine (DPG), Zn-2-mercaptobenzo thiazole (ZMBT) and sulfur were the grades customarily used in rubber industry.

Formulations and mixing

A masterbatch of hybridized precipitated silica-calcined clay NR/EPDM/SBR blend added with TESPT (SiCyMB) was prepared as Table 1 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 at temperature 130 ^{0}C and mixing time of 14 minutes. SiCyMB is used as reinforcing filled masterbatch in the industry of producing rubber molded mat. Besides, a main masterbatch (NRMain) was prepared as Table 1 by using a laboratory scale two-roll-mill (Radicon) with a friction ratio of 1.25 at temperature 40 ^{0}C. The nip of the rollers was adjusted during mixing and the compound was cut and folded by using a cutter knife.

Table 1: Formulation of SiCyMB and NRMain

Ingredient	SiCyMB (phr[a])	NRMain (phr[a])
NR	67.65	100.00
EPDM	19.03	-
SBR	13.32	-
Paraffinic oil	6.09	0.50
Precipitated silica	10.66	-
Calcined clay	19.79	-
Homogenizing resin	3.04	-
Metal soap	3.81	-
TESPT	6.09	-
Phenolic antioxidant	-	0.25
ZnO	-	4.80
Stearic acid	-	3.00
Polyethylene glycol	-	3.00
Titanium dioxide	-	4.50
Total	149.48	116.05

[a]Part per hundred rubber

NRMain and SiCyMB were then subjected for final two-roll-mill mixing added with rubber accelerators (MBTS and DPG) and sulfur in sequent at temperature 40 ^{0}C for a mixing time of 10 minutes. This final compound was mixed in monthly basis for 6 months continuously. The percentage ingredients for these mixings are depicted in Table 2. Using of materbatches mixing method in present study is intended to prevent mixing variation throughout the time factor.

Table 2: Percentage ingredients of final mixing

Ingredient	Percentage (%)
NRMain	64.1
SiCyMB	32.0
MBTS	2.2
DPG	0.1
Sulfur	1.6
Total	100.00

Determination of Cure Characteristics

Cure characteristics were determined by using an oscillating rotorless rheometer (UR2010) from U-CAN Dynatex Inc., Taiwan. The upper and lower dies were set to 165 °C and 4.5 kg/cm^2 of pressure for 240 sec. in compliance with ASTM D5289. The final compound was conditioned at room temperature for 24 hours each time before the testing. The data of cure characteristics for scorch time (T_2), 90 % cure time (T_{90}) and cure rate index (CRI) were recorded for every tested compound. CRI, which is a measure of cure reaction is given as Equation 1 [15]:

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

Total 6 data (1st - 6th month) of T_2 and CRI were recorded throughout 6 months of storage period at the ambient temperature of 24-28 ^{0}C. Statistical correlation techniques were performed on the degrees of relationship between the storage period of SiCyMB over the data of T_2 and CRI. 6 months of storage (X) is regarded as an independent variable whereas T_2 and CRI (Y) are both dependent variables. Pearson correlation (r) that measures the degree and direction of linear relationship between two variables was calculated by using Equation 2 [17]:

$$\text{Calculated } r = \frac{(n.\Sigma XY)-(\Sigma X. \Sigma Y)}{\sqrt{[(n.\Sigma X^2)-(\Sigma X)^2] \times [(n.\Sigma Y^2)-(\Sigma Y)^2]}} \tag{2}$$

Degree of freedom, df = n-2

Value r is the correlation coefficient which is a measure of the strength of relationship. Closer the value gets to either +1.0 or -1.0, stronger the association [16]. Degree of freedom (df = n-2$)$ was recorded as 4 (df = 6-2) of which the critical r was determined as 0.811 (Pearson's r Table) at the significant level of two-tailed test at 0.05. Fourier-transform infrared (FTIR) spectroscopy was carried out by using a machine of model Spectrometer 6700. Attenuated total reflectance (ATR) spectroscopy was used to analyze the spectra of the vulcanizates produced in 1st, 3rd and 6th months in the range of 500–4000 cm^{-1} to observe the possible changes of chemical bonding vibration throughout the prolonged storage in supporting the findings of cure characteristics with regard to the trend of premature cure.

Determination of Bound Rubber Content (BRC)

Test of BRC was performed on the SiCyMB in monthly basis started from the month of producing and throughout 6 months of ambient storage (7 data). 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 [10]:

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

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.

Results and Discussion

Table 3: The 6 months data and calculated r of T_2 and CRI

T$_2$					CRI				
Storage Period, Month (X)	X^2	T$_2$, Sec. (Y)	Y^2	XY	Storage Period, Month (X)	X^2	CRI min^{-1} (Y)	Y^2	XY
1	1	76.67	5878.29	76.67	1	1	129.11	16669.39	129.11
2	4	80.00	6400.00	160.00	2	4	123.30	15202.89	246.60
3	9	81.33	6614.57	243.99	3	9	123.44	15237.43	370.32
4	16	75.00	5625.00	300.00	4	16	133.40	17795.56	533.60
5	25	75.00	5625.00	375.00	5	25	129.51	16772.84	647.55
6	36	78.33	6135.59	469.98	6	36	129.67	16814.31	778.02
Sum (Σ) 21	91	466.33	36278.45	1625.64	21	91	768.43	98492.42	2705.20

Calculated r for T_2:

$$= \frac{6(1625.64) - (21 \times 466.33)}{\sqrt{[(6 \times 91) - (21)^2] \times [(6 \times 36278.45)-(466.33)^2]}}$$

$$= -0.26$$

Calculated r for CRI:

$$= \frac{6(2705.20) - (21 \times 768.43)}{\sqrt{[(6 \times 91) - (21)^2] \times [(6 \times 98492.42)-(768.43)^2]}}$$

$$= 0.42$$

Critical r (2-tailed test at 0.05) = 0.811   Critical r (2-tailed test at 0.05) = 0.811

Premature Cure

Correlation analyses were performed for the degree of relationship between prolonged 6 months storage at ambient temperature (24-28 ^{0}C) for the final compounds over T_2 and CRI. The results and calculated r (as Equation 2) of T_2 and CRI are depicted in Table 3.

The calculated r of T_2 and CRI are -0.26 and 0.42 respectively and both figures are smaller than the critical r of 0.811. Since critical r > calculated r, it is concluded that no significant correlations between 6 months storage over T_2 and CRI and thus hypothesis null is accepted. In this perspective, no premature cure takes place for SiCyMB although it is added with TESPT compounded by using high temperature 130 ^{0}C internal melt mixing method. Although the sulfide groups of TESPT may serve as sulfur donor in instigating premature-cured reactions with rubber matrix, however it is not in corresponding with the present statistical correlations on T_2 and CRI. It is inferred that no remarkable reactions between the tetrasulfide of TESPT with rubber chains throughout 6 months of ambient storage. From this standpoint, it asserts that forming of rubber-filler linkages only occurs at high molding temperature. Zloczower [17] reported that sufficient temperature at the vicinity of 160 ^{0}C is needed for the polysulfide of silane reacting with rubber molecules. Moreover, Debnath et al. [13] claimed that tetrasulfide of TESPT reacts with rubber at the temperature of above 120 ^{0}C forming rubber-silica chemical bonds but lies below this temperature, the reaction rate is relatively low or even no reaction takes place at all. Figure 1 exhibits the FTIR spectra obtained for the storage of one, three and six month(s) for SiCyMB.
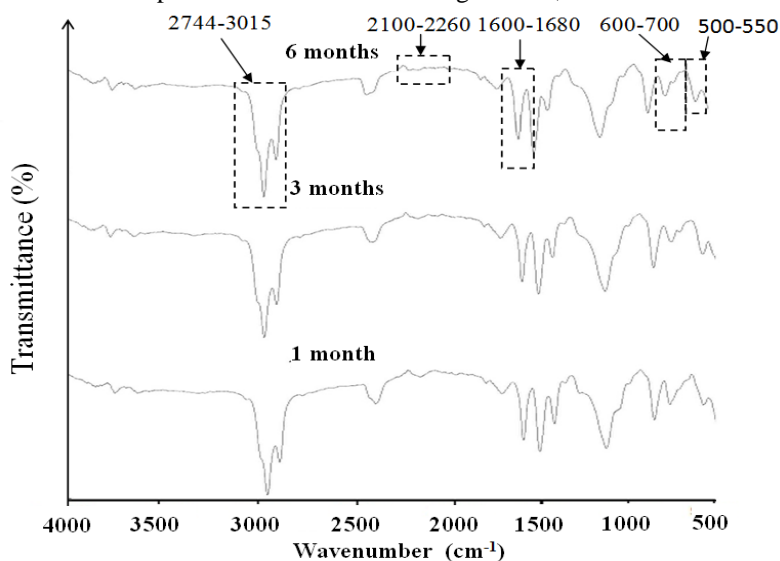

Figure 1: FTIR spectra of CSNMB conditioned for one, three and six month(s)
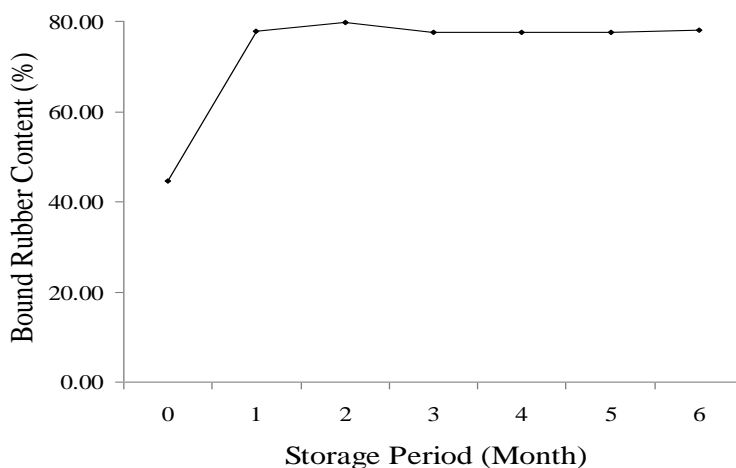

Storage period (Month)	0	1	2	3	4	5	6
BRC (%)	44.50	77.88	79.72	77.55	77.64	77.49	78.09

Figure 2: BRC of SiCyMB throughout 6 months of storage

It is evident that the spectra throughout 6 months storage do not exhibit significant differences across the peak range of 500-4000 cm^{-1}. No significant differences at the peaks of 2744-3015 cm^{-1} for the aliphatic symmetric and asymmetric C-H stretching. No dramatic differences at 1600-1680 cm^{-1} and 2100-2260 cm^{-1} for C=C stretching imply consistent saturation levels of vulcanizates throughout the storage. In addition, no significant differences on the sulfuric crosslinks of C-S and S-S stretching at the peaks of 600-700 cm^{-1} and 500-550 cm^{-1} respectively assert consistency of compound cure behavior for SiCyMB.

Bound Rubber Content (BRC)

Figure 2 demonstrates the BRC of SiCyMB with significant increase after one month of storage at ambient temperature.

A dramatic increase until 77.88 % from the initial 44.50 % is observed which represents a remarkable 75.01 % of enhancement. However, no significant differences are observed thereafter with an average fluctuation at 77-79 %. The trend of change manifests an increase on rubber-filler interaction of SiCyMB through time until achieving an equilibrium level within the first month. As claimed by Choi [18], BRC for the silica-filled rubber added with organosilane increases through storage time due to further reaction of silane with silica even at low storage temperature of 30 ^{0}C. Moreover, Leblanc [19] cited bound rubber of after-mixed rubber is increased upon storage until reaching an equilibrium value attributable to the displacement of short rubber segments into longer chains that increases bound rubber. Thus, it is inferred that enhancement of BRC throughout prolonged storage is contributed by the continuous forming of silane-filler chemical linkages together with the increasing of rubber molecular weight during compound resting.

Conclusion

No premature cure for the SiCyMB when conditioning it at prolonged 6 months of ambient storage. SiCyMB produced by high mixing temperature is evidently does not reveal significant correlation between the storage time against the premature cure behavior investigated through statistical correlation r analyses. This feature serves as an advantage to rubber industry which may require the high temperature-mixed silanized compounds being subjected for prolonged storage. With regards to BRC, SiCyMB manifests a dramatic increase after it is conditioned to 1 month storage which supports the enhanced rubber-filler interaction and increased molecular weight of rubber during ambient storage of compound at 24-28 ^{0}C.

Acknowledgements

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