SCIENCE DILIMAN (JULY-DECEMBER 2014) 26:2, 21-39

Effect of Ingredient Loading on Surface Migration Kinetics of Additives in Vulcanized Natural Rubber Compounds

Bryan B. Pajarito*
Christia Angeline de Torres
Marienne Maningding
University of the Philippines Diliman

ABSTRACT

Surface migration kinetics of chemical additives in vulcanized natural rubber compounds were studied as function of ingredient loading. Rubber sheets were compounded according to a 2^{12-8} fractional factorial design of experiment, where ingredients were treated as factors varied at two levels of loading. Amount of migrated additives in surface of rubber sheets was monitored through time at ambient conditions. The maximum amount and estimated rate of additive migration were determined from weight loss kinetic curves. Attenuated total reflection–Fourier transform infrared (ATR-FTIR) spectroscopy and optical microscopy were used to characterize the chemical structure and surface morphology of sheet specimens during additive migration. ANOVA results showed that increased loading of reclaimed rubber, $CaCO_3$, and paraffin wax significantly decreased the maximum amount of additive migration; by contrast, increased loading of used oil, asphalt, and mercaptobenzothiazole disulphide (MBTS) increased the maximum amount. Increased loading of sulfur, diphenylguanidine (DPG), and paraffin wax significantly decreased the additive migration rate; increased loading of used oil, asphalt, and stearic acid elicited an opposite effect. Comparison of ATR-FTIR spectra of migrated and cleaned rubber surfaces showed significant variation in intensity of specific absorbance bands that are also present in infrared spectra of migrating chemicals. Paraffin wax, used oil, stearic acid, MBTS, asphalt, and zinc stearate were identified to bloom and bleed in the rubber sheets. Optical micrographs of migrated rubber surfaces revealed formation of white precipitates due to blooming and of semi-transparent wet patches due to bleeding.

Keywords: Rubber, migration, blooming, bleeding, vulcanizate, ingredient loading

---

*Corresponding Author

ISSN 0115-7809 Print / ISSN 2012-0818 Online

INTRODUCTION

Rubber compounds are mixtures made of a matrix based on one or more types of raw gum elastomer and dispersed amounts of different chemical ingredients. These ingredients include vulcanizing agents, activators, accelerators, fillers, antidegradants, processing aids, and other additives designed to modify and convert the raw gum elastomer matrix into a useful material. During compounding, selected ingredients are added to the rubber matrix at specific loadings to achieve good processing characteristics, yield the best balance of physical properties, lower the price of formulation, and even limit the hazard of the desired compound and rubber end-product to health, safety, and environment (Dick 2009).

However, when high loadings of ingredients are mixed to the rubber matrix, some of the chemical additives migrate from the bulk matrix to the surface of the rubber because of oversaturation and limited solubility. In most cases, the migrated additives accumulate at the surface and form solid precipitates, resulting in a bloom. According to literature, a large number of compounding ingredients are known to migrate and bloom in rubber. These include sulfur (Venable and Greene 1922, Auerbach and Gehman 1954, Wake and others 1983, Jurkowski and Jurkowska 1998, Ciesielski 1999, Mark and others 2005, Bart 2006, Dick 2009, Basak and others 2010, Dick 2014); activators such as zinc oxide (Wake and others 1983, Saeed and others 2011, Saeed and others 2012a and 2012b, Dick 2014) and stearic acid (Sugiura and others 1996, Bielinski and others 2005, Dick 2009); antidegradants such as wax (Nah and Thomas 1980, Wake and others 1983, Choi 1999a and 1999b, Ciesielski 1999, Mark and others 2005, Bart 2006, Dick 2009, Torregrossa-Coque and others 2011a and 2011b, Dick 2014), paraphenylenediamines (Wake and others 1983, Choi 1997, 1998, 1999a, and 1999b, Parra and others 2000, Mark and others 2005, Bart 2006, Dick 2009, Saeed and others 2011, Saeed and others 2012a and 2012b, Dick 2014), and butylated hydroxytoluene (Keen and others 1992, Choi 1997 and 1998); and various accelerators such as dithiocarbamates (zinc dimethyl-, diethyl-, and dibutyl- salts), thiazoles (mercaptobenzothiazole and its disulfide), sulfenamides (tert-butyl-benzothiazole sulfenamide), and thiurams (tetramethylthiuram mono- and disulfide) (Wake and others 1983, Bart 2006, Dick 2009, Saeed and others 2011, Torregrossa-Coque and others 2011a and 2011b, Saeed and others 2012a and 2012b, Dick 2014). The high loading of process oils and plasticizers in the rubber matrix also results in migration and surface bleeding, leading to a wet and oily bloom (Wake and others 1983, Sugiura and others 1996, Bart 2006, Dick 2009 and 2014). Antidegradants are designed to deliberately migrate to the rubber surface and create a passive barrier against ozone attack (Wake and others 1983, Choi 1997, 1998, and 1999, Ciesielski 1999, Dick 2009); nevertheless, the undesirable deposition of other migrated additives at the surface can cause several problems. The appearance of a bloom at the rubber surface is visually offensive and can cause rejection and return of the rubber product. It destroys building tack and interferes with the adhesion of rubber to other material surfaces (Wake and others 1983, Ciesielski 1999, Dick 2009 and 2014). Human contact to bloom can also cause skin irritation (Bart 2006). Blooming can also facilitate the initiation of cracks at the reagglomeration sites and reduce the fatigue life of rubber because of the reagglomeration of additives at the surface and in bulk (Saeed and others 2011).

The migration of chemical additives in rubber is related to diffusion kinetics, and is dependent on several factors such as additive-rubber compatibility, molecular size of migrating additive, physical and chemical interactions between additive and rubber molecules, configuration of rubber chains and voids, and others (Bart 2006). Loading a rubber matrix with a soluble ingredient beyond its solubility limit is already established to cause the excess amount to simply migrate and bloom or bleed at the surface. However, the effect of insoluble and/or non-migrating compounding ingredients to the blooming and bleeding behavior of soluble additives in rubber has scarcely been investigated. Sugiura and others (1996) reported that loading ethylene-propylene diene monomer (EPDM) rubber with sepiolite, a clay mineral and adsorbent, prevents blooming and bleeding of paraffin process oil, stearic acid, and curing product zinc stearate at the rubber surface. Choi (1998) showed that increased loading of silica filler in natural rubber vulcanizates reduce the migration rates of butylated hydroxytoluene, paraphenylenediamines, and wax. Talc, a semi-reinforcing filler, was also reported to reduce iridescent bloom (Dick 2014). The effect of loading other insoluble and/or non-migrating compounding ingredients such as reclaimed rubber, calcium carbonate, kaolin clay, and asphalt in the blooming and bleeding of oversaturated additives in rubber is not yet investigated.

This work studied surface migration kinetics of chemical additives in vulcanized natural rubber compounds as a function of ingredient loading. A fractional factorial design was used during the formulation of rubber compounds, where ingredients were assigned as factors and were varied at two different loadings. In experimental design, reclaimed rubber, calcium carbonate, kaolin clay, and asphalt were treated as unconfounded factors, whereas the remaining ingredients were assigned as factors confounded with two- or more factor interactions. The amount of migrated additives at the surface of rubber sheet specimens was monitored through time at ambient conditions. Mean effects and factor ranking were calculated and performed from the results. ANOVA was used to determine the compounding ingredients that have a significant effect on blooming and bleeding behavior. Attenuated total reflection–

Fourier transform infrared (ATR-FTIR) spectroscopy and optical microscopy were used to identify the migrating additives and to characterize the surface morphology of rubber sheet specimens during blooming and bleeding, respectively.

METHODOLOGY

Table 1 shows the basic and the selected upper and lower loadings of compounding ingredients used in the formulation of rubber sheet specimens. Ingredient loading was expressed as parts per hundred (phr) parts of Standard Philippine Rubber (SPR 20). Reclaimed rubber is vulcanized scrap rubber recovered from grinded tire threads and is chemically treated. It is also commonly used as an economical filler for natural rubber. Asphalt is an inexpensive tackifier. Calcium carbonate and kaolin clay are non-black fillers for cost reduction and hardness improvement. As seen in Table 1, sulfur was used as the vulcanizing agent, zinc oxide and stearic acid as the activators, paraffin wax as an antidegradant, petroleum oil as a processing aid, and mercaptobenzothiazole disulfide (MBTS), mercaptobenzothiazole (MBT), and diphenylguanidine (DPG) as the accelerator system. Each ingredient was assigned as a factor X_i varied at two levels of loading (upper and lower) relative from their respective basic loading.

Table 1. Basic, upper, and lower loadings of compounding ingredients in rubber formulations

Ingredient loading, phr	Reclaimed rubber, X_1	$CaCO_3$, X_2	Kaolin clay, X_3	Asphalt, X_4	ZnO, X_5	Stearic acid, X_6
Basic	33	400	35	3.0	6	1.5
Variation interval	15	100	15	1.5	3	1.0
Upper	48	500	50	4.5	9	2.5
Lower	18	300	20	1.5	3	0.5

Ingredient loading, phr	Paraffin wax, X_7	Used oil, X_8	Sulfur, X_9	MBTS, X_{10}	MBT, X_{11}	DPG, X_{12}
Basic	2.5	95	2.5	1.5	1.5	1.5
Variation interval	1.5	25	1.5	1	1	1
Upper	4	120	4	2.5	2.5	2.5
Lower	1	70	1	0.5	0.5	0.5

To evaluate the effect of ingredient loading on the migration kinetics of additives at the surface of rubber sheets, eighteen natural rubber compounds were prepared at different ingredient loading combinations. The formulations are given in Table 2.

The coded value of the *i*-th factor ingredient X_i in the table is calculated by the equation (upper or lower loading – basic loading) $\cdot$(variation interval)$^{-1}$. A value of X_i = +1 corresponds to the upper loading of *i*-th factor ingredient; X_i = -1 for the lower loading, and X_i = 0 for the basic loading (Lazic 2004). For example, rubber compound 1 in Table 2 was formulated using 18 parts reclaimed rubber, 300 parts $CaCO_3$, 20 parts kaolin clay, 1.5 parts asphalt, 9 parts ZnO, 0.5 parts stearic acid, 1 part paraffin wax, 120 parts used oil, 1 part sulfur, 2.5 parts MBTS, 2.5 parts MBT, and 0.5 part DPG per 100 parts of natural rubber.

Table 2. Formulations of rubber compounds

Compound Number	Factor ingredients											
	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	X_9	X_{10}	X_{11}	X_{12}
1	-1	-1	-1	-1	+1	-1	-1	+1	-1	+1	+1	-1
2	-1	-1	-1	+1	-1	+1	+1	-1	+1	-1	-1	-1
3	-1	-1	+1	-1	-1	+1	+1	-1	-1	+1	+1	+1
4	-1	-1	+1	+1	+1	-1	-1	+1	+1	-1	-1	+1
5	-1	+1	-1	-1	-1	+1	-1	+1	+1	-1	+1	+1
6	-1	+1	-1	+1	+1	-1	+1	-1	-1	+1	-1	+1
7	-1	+1	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1
8	-1	+1	+1	+1	-1	+1	-1	+1	-1	+1	-1	-1
9	+1	-1	-1	-1	-1	-1	+1	+1	+1	+1	-1	+1
10	+1	-1	-1	+1	+1	+1	-1	-1	-1	-1	+1	+1
11	+1	-1	+1	-1	+1	+1	-1	-1	+1	+1	-1	-1
12	+1	-1	+1	+1	-1	-1	+1	+1	-1	-1	+1	-1
13	+1	+1	-1	-1	+1	+1	+1	+1	-1	-1	-1	-1
14	+1	+1	-1	+1	-1	-1	-1	-1	+1	+1	+1	-1
15	+1	+1	+1	-1	-1	-1	-1	-1	-1	-1	-1	+1
16	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
17	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
18	0	0	0	0	0	0	0	0	0	0	0	0

The ingredient loading combinations for compounds 1–16, as shown in Table 2, were derived from a 2^{12-8} fractional factorial design of experiment (Lazic 2004). The design matrix was generated from the *fracfactgen* and *fracfact* functions of Matlab 6.5 using 12 main factor terms, with k = 4 for 2^k runs under design resolution 3. The total number of runs or formulations (2^k = 16) of the generated design matrix corresponds to 1/256 fraction of a 2^{12} full factorial experiment. The first four factor ingredients (reclaimed rubber, $CaCO_3$, kaolin clay, and asphalt) were unconfounded, whereas the effects of the remaining factor ingredients were confounded with factor interactions. The confounding factor interactions are given by the following generating ratios:

$$X_5 = X_1X_2X_3X_4 \quad (1)$$
$$X_6 = X_2X_3X_4 \quad (2)$$
$$X_7 = X_1X_3X_4 \quad (3)$$
$$X_8 = X_3X_4 \quad (4)$$
$$X_9 = X_1X_2X_4 \quad (5)$$
$$X_{10} = X_2X_4 \quad (6)$$
$$X_{11} = X_1X_4 \quad (7)$$
$$X_{12} = X_1X_2X_3. \quad (8)$$

Thus, if E and E' are the true and estimated factor effects to an experimental response, respectively, the estimated effect of reclaimed rubber E'_{X1} is equal to E_{X1} because it is unconfounded; on the other hand, the estimated effect of paraffin wax E'_{X7} is equal to $E_{X7} + E_{X1X3X4}$, where E_{X1X3X4} is the effect due to three-way factor interaction of reclaimed rubber, kaolin clay, and asphalt. Compounds 17 (all ingredients are at low loading) and 18 (all ingredients are at basic loading) were also formulated for comparison.

Rubber compounds listed in Table 2 were mixed in a heated two roll mill. All ingredients were added on the first batch of mixing, except sulfur and the accelerator system. The resulting master batch was aged for 24 hrs at ambient conditions before roll milling with sulfur and accelerators. Compounds were then cured using a heated compression molding press at 160 °C for 20 mins. The vulcanized rubber sheets have final dimensions of 300 mm × 300 mm × 3 mm. The preparation of ingredients, compounding, and vulcanization of rubber sheets were performed by Rhodeco Rubber Processing Services, Inc.

Rubber sheet specimens of 50 mm × 50 mm × 3 mm size were cut from the vulcanized sheets. The migration experiments were performed in open air at ambient conditions for 32 d. Sheet specimens were clipped and left hanging in a metal rack to allow unhindered migration of additives to the exposed surface. The amount of additives that migrated to the surface of the rubber sheet specimens were determined by periodically removing the additives that have bloomed and bled to the surface, and measuring the weight loss (Nah and Thomas 1980). The removal was done by means of a single pass of adhesive tape (Scotch tape). Percent weight loss due to additive migration M_t in rubber sheet specimens was calculated by:

$$M_t = \frac{W_i - W_t}{W_i} \times 100 \quad (1)$$

where W_i is the initial weight of the rubber sheet specimen and W_t is the weight of the rubber sheet specimen after application of adhesive tape at time *t*. Using Equation 1, the total amount of additives that migrated to the surface of specimens were recorded as a function of time. Three specimens from each compound were used to report the average weight loss.

Other rubber sheet specimens were left unmonitored for 32 d, and their migrated surfaces were analyzed using ATR-FTIR spectroscopy and optical microscopy. Afterwards, the migrated surfaces were cleaned with adhesive tape, and the resulting infrared spectra were recorded. For comparison and possible identification of migrating additives, ATR-FTIR spectra of compounding ingredients were also measured.

RESULTS AND DISCUSSION

Figures 1–3 illustrate the amount of additive migration in terms of cumulative weight loss in rubber sheet specimens as a function of time. All compounds exhibit an increasing amount of migrating additives to the rubber surface through observation time at ambient conditions. Moreover, the migration kinetic curves have non-zero weight loss value at $t = 0$, indicating the presence of migrated additives at the specimen surface before the migration experiments were started. In terms of maximum amount of additive migration, compounds 1, 8, and 4 (0.59%, 0.57%, and 0.48%, respectively) exhibited the highest amount, whereas compounds 14, 18, and 17 (0.13%, 0.14%, and 0.15%, respectively) exhibited the lowest amount, after 32 d

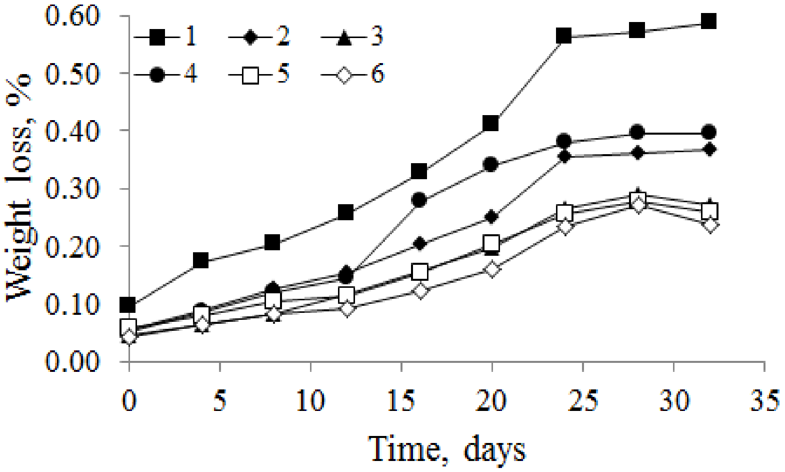

Figure 1. Migration kinetic curves of additives in rubber compounds 1–6.

of migration. Aside from determining the maximum amount of additive migration, the migration rate was also measured from the initial slope of the kinetic curves. The migration rate was calculated as the slope of the regressed line using data points of the kinetic curves at $t = 0$, 4, and 8 d. From this procedure, compounds 8, 1, and 10 ($2.80 \times 10^{-2}\% \cdot d^{-1}$, $1.38 \times 10^{-2}\% \cdot d^{-1}$ and $1.30 \times 10^{-2}\% \cdot d^{-1}$, respectively) were found to have the highest migration rate, whereas compounds 17, 14, and 18 ($3.9 \times 10^{-3}\% \cdot d^{-1}$, $4.0 \times 10^{-3}\% \cdot d^{-1}$, $4.3 \times 10^{-3}\% \cdot d^{-1}$, respectively) have the lowest rate. Figures 4 and 5 illustrate the effect of ingredient loading on the maximum amount

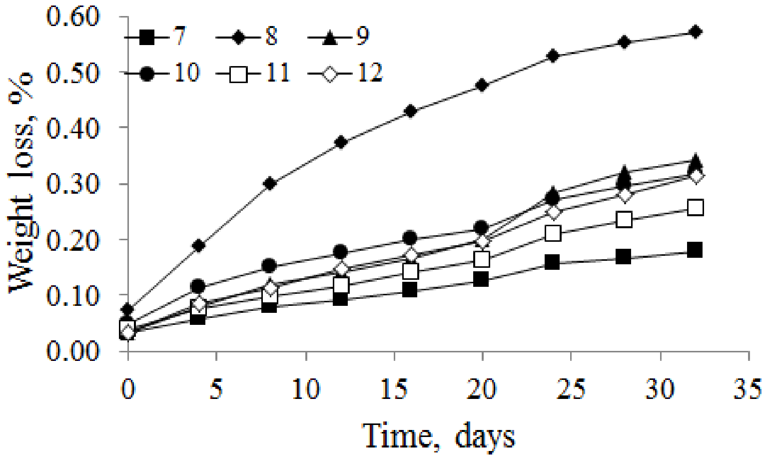

Figure 2. Migration kinetic curves of additives in rubber compounds 7–12

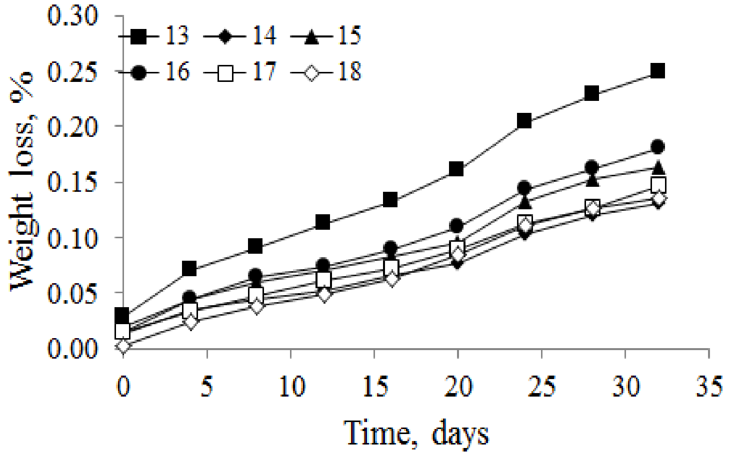

Figure 3. Migration kinetic curves of additives in rubber compounds 13–18

and the rate of additive migration on surfaces of rubber sheet specimens, respectively. The bars indicate the mean values of maximum amount and rate of additive migration at low and high ingredient loadings. The mean values were calculated using Table 2. For example, let y_j be the maximum amount of additive migration of *j*-th rubber compound. Following the coded values of factor ingredients in Table 2, the mean value of maximum amount of migration at low loading $\overline{y}_{\text{low}}$ of reclaimed rubber (X_1) was computed as:

$$\overline{y}_{\text{low}} = \frac{y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 + y_{17}}{9} \qquad (2)$$

Likewise, the mean value at high loading $\overline{y}_{\text{high}}$ of reclaimed rubber was:

$$\overline{y}_{\text{high}} = \frac{y_9 + y_{10} + y_{11} + y_{12} + y_{13} + y_{14} + y_{15} + y_{16}}{8} \qquad (3)$$

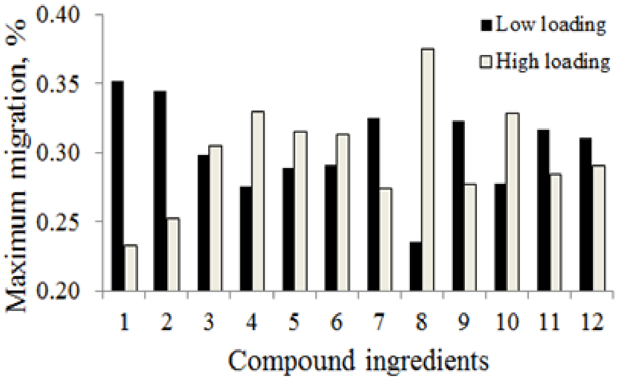

Figure 4. Effect of ingredient loading on maximum amount of additive migration.

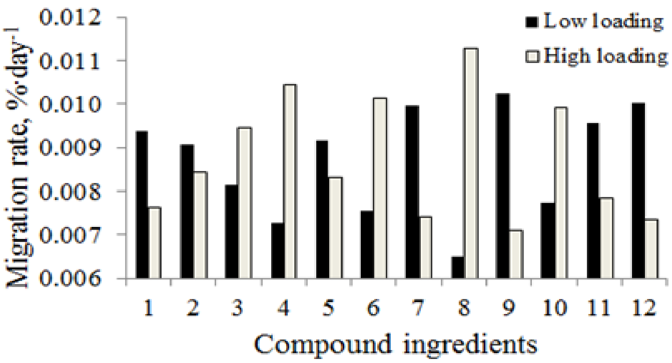

Figure 5. Effect of ingredient loading on surface migration rate of additives.

The mean values at low and high loading of *i*-th compounding ingredient were calculated following the distribution of coded values of X_i (-1 for low, +1 for high loading) in Table 2.

In Figure 4, the maximum amount of additive migration in rubber sheet specimens was observed to increase when the following compounding ingredients were increased in loading in the formulations: kaolin clay, asphalt, zinc oxide, stearic acid, used oil, and MBTS. By contrast, increased loading of reclaimed rubber, $CaCO_3$, paraffin wax, sulfur, MBT, and DPG in the rubber formulations resulted to decrease in maximum amount of additive migration in rubber sheet specimens.

In Figure 5, the migration rate of additives to the rubber surface was found to be enhanced when loading of kaolin clay, asphalt, stearic acid, sed oil, and MBTS were increased in the formulations. However, high loading of reclaimed rubber, $CaCO_3$, ZnO, paraffin wax, sulfur, MBT, and DPG in the formulations was observed to decrease the migration rate of additives.

Using the mean values at low and high ingredient loadings, as seen in Figures 4 and 5, the estimated effect of factor ingredients on maximum amount and rate of surface migration of additives in rubber sheet specimens were quantified, and were used to rank the ingredients according to the magnitude of estimated effect. These are shown in Figures 6 and 7. The bars in Figures 6 and 7 demonstrate the effect *E'* of each compounding ingredient on maximum amount and rate of migration, expressed as:

$$E' = \frac{\bar{y}_{\text{high}} - \bar{y}_{\text{low}}}{\bar{y}_{\text{low}}} \times 100 \qquad (4)$$

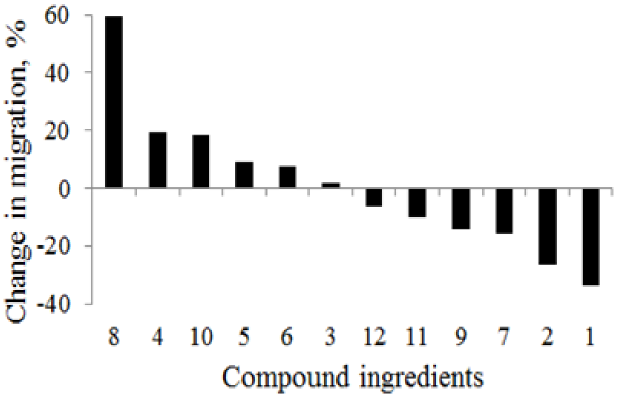

Figure 6. Ranking of compounding ingredients in terms of their effect on maximum amount of additive migration.

As shown in Figure 6, used oil, asphalt, and MBTS have the highest effect in increasing the maximum amount of additive migration (59.6%, 19.5%, and 18.4%, respectively) among the compounding ingredients. On the other hand, reclaimed rubber, $CaCO_3$, and paraffin wax have the largest effect in decreasing the maximum amount of additive migration (-33.9%, -26.7%, and -15.8%, respectively). ANOVA using Matlab's *anovan* function reveals that the effect of these compounding ingredients was statistically significant at a 95% confidence level. Likewise, in Figure 7, ingredients such as used oil, asphalt, and stearic acid have the greatest effect in enhancing the rate of additive migration (73.3%, 43.3%, and 34.4%, respectively), whereas sulfur, DPG, and paraffin wax have the highest effect in lowering the migration rate (-30.4%, -26.5%, and -25.6%, respectively). The observed effects of these ingredients on migration rate were also found to be statistically significant at a 95% confidence level.

In terms of increased additive migration, high levels of processing oils, stearic acid, and MBTS in rubber recipes are known to cause blooming and bleeding (Sugiura and others 1996, Bielinski and others 2005, Bart 2006, Dick 2009 and 2014). Asphalt, commonly used as building material in roofing and paving applications, is a natural organic end-product subject to chemical oxidation through reactions with atmospheric oxygen (Petersen 2009). Increased loading of asphalt in rubber compounds may have caused a pseudo bloom (Wake and others 1983), as observed from black specks found in adhesive tapes used during the late stages of migration experiments.

With respect to the effect of the other significant ingredients, the decrease in migration rate due to high loading of sulfur and DPG can be attributed to increased cured modulus and ultimate crosslink density (Dick 2014), resulting in slow diffusion

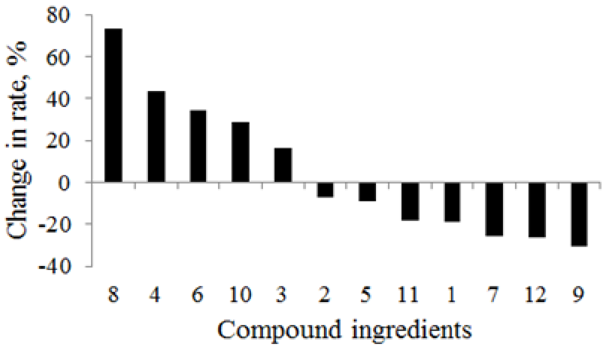

Figure 7. Ranking of compounding ingredients in terms of their effect on surface migration rate of additives.

of additives from bulk to the surface of the rubber sheet. The observed decrease in additive migration due to high loading of wax can be explained by the interface between the wax bloom and the surface of the rubber vulcanizate. Choi (1999) found the surface migration of paraphenylenediamines in natural rubber vulcanizates compounded with wax to be slower and lower than those in vulcanizates without wax. A discontinuous concentration gradient of migrating additives was observed at the bloom-vulcanizate interface, where higher concentration of additives is found at the interface than at the bulk regions of the rubber and wax bloom. The wax bloom impeded migration and caused accumulation of migrating additives at the bloom-vulcanizate interface. Meanwhile, the increased loading of $CaCO_3$ reduced migration through an increased diffusion path length of migrating additives from bulk to the surface of rubber sheet. Lastly, high loading of reclaimed rubber in the formulation extended the rubber matrix greatly and contributed to the absorption and retention of migrating additives.

Figures 8 and 9 show the ATR-FTIR spectra of the rubber sheet specimens after 32 d of additive migration at ambient conditions. High absorption bands were found at wave numbers 500 cm^{-1} – 1600 cm^{-1} and 2800 cm^{-1} – 3000 cm^{-1}; nevertheless, not all compounds exhibited significant peaks at the latter wave number range (see ATR-FTIR spectra of compound 4 in Figure 8; compounds 11 and 14–18 in Figure 9). Migrated surfaces of rubber sheet specimens were then cleaned several times with adhesive tape to ensure removal of migrated additives. For each compound, the ATR-FTIR spectrum of the cleaned surface was measured and superimposed to the

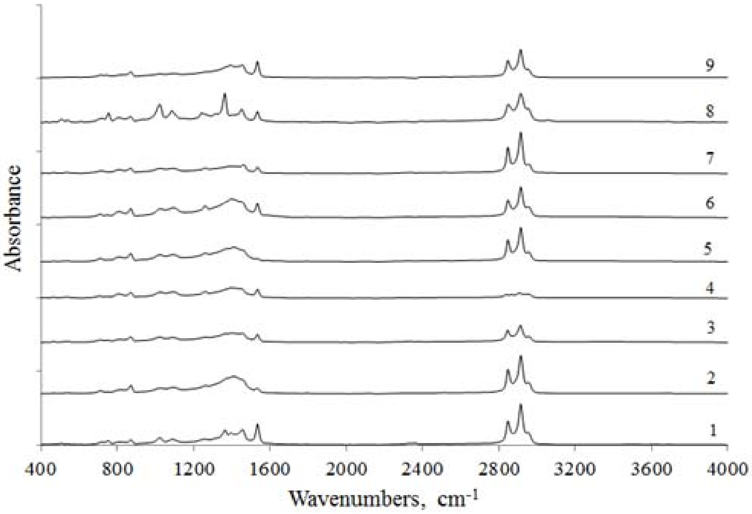

Figure 8. ATR-FTIR spectra of migrated rubber surfaces for compounds 1–9.

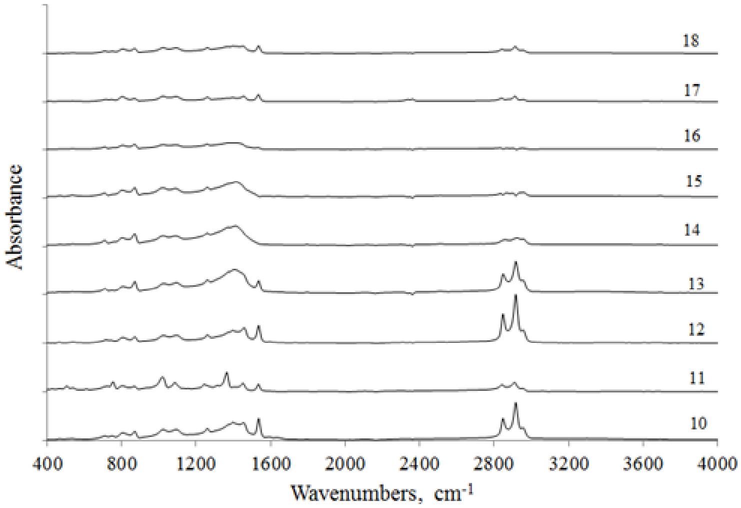

Figure 9. ATR-FTIR spectra of migrated rubber surfaces for compounds 10–18.

infrared spectrum of the migrated surface. The superimposed spectra were manually compared to indicate changes in position and intensity of absorption bands. Figures 10 and 11 illustrate this procedure for compounds 1 and 15, respectively. In Figure 10, decrease in band intensity at wave numbers 2916 cm^{-1}, 2848 cm^{-1}, and 1535 cm^{-1} were observed after the removal of bloom and bleed in the rubber surface. Moreover, absorption bands at 1455 cm^{-1} and 1397 cm^{-1} disappeared after cleaning. In some specimens, such as compound 15 in Figure 11, new absorption bands with high intensity emerged at 2916 cm^{-1} and 2848 cm^{-1}, accompanied by disappearance of the band at 1257 cm^{-1} after removal of migrated additives. The ATR-FTIR spectra of compounding ingredients shown in Figures 12 and 13 were also used as reference to identify the migrated additives.

Based on the superimposed ATR-FTIR spectra of cleaned and migrated rubber surfaces, as well as the measured spectra of compounding ingredients, the following absorption bands were found to be characteristic of the migrated additives in rubber compounds (Sugiura and others 1996): 2954 cm^{-1}, 2916 cm^{-1}, and 2848 cm^{-1} for antisymmetric and symmetric CH stretching of wax, used oil, and stearic acid; 1535 cm^{-1} and 1397 cm^{-1} for asymmetric and symmetric -COO- stretching of zinc stearate, the reaction product of ZnO and stearic acid; 1455 cm^{-1} for antisymmetric CH deformation of wax, used oil, and stearic acid; 1257 cm^{-1} for CO stretch of stearic acid; and 724 cm^{-1} for $-CH_2-$ rocking and wagging of wax, used oil, and stearic acid. Absorption bands found in asphalt (1095 cm^{-1} and 1025 cm^{-1}) and MBTS (755 cm^{-1}) also exhibited changes in band intensity after cleaning of migrated rubber surfaces.

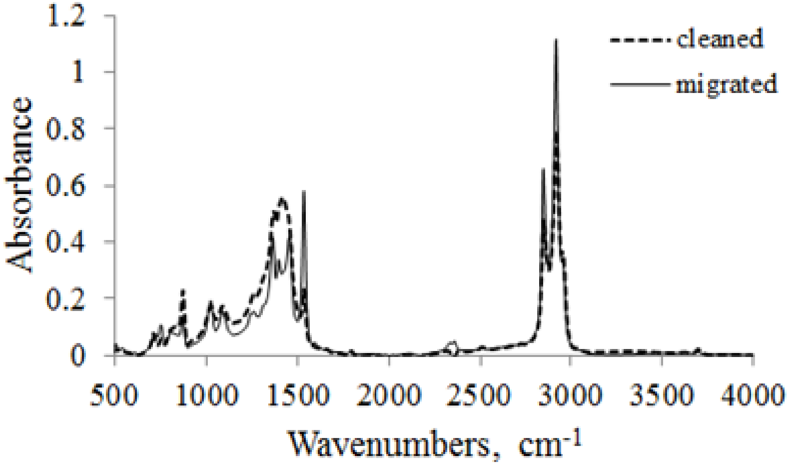

Figure 10. ATR-FTIR spectra of cleaned and migrated rubber surfaces of compound 1.

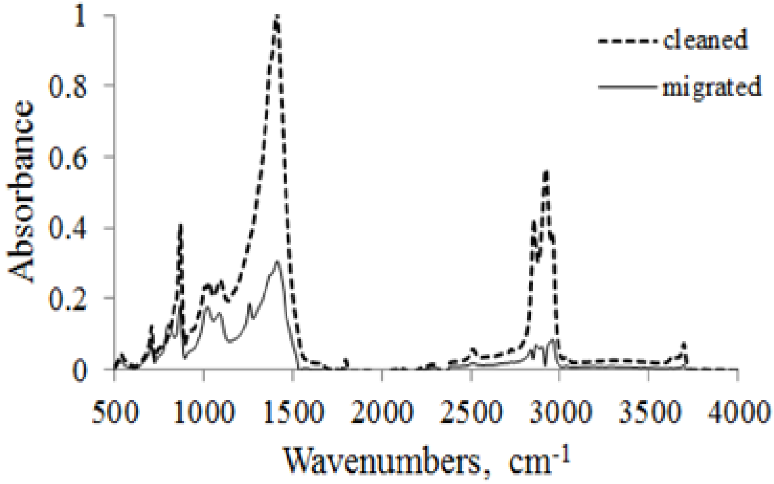

Figure 11. ATR-FTIR spectra of cleaned and migrated rubber surfaces of compound 15.

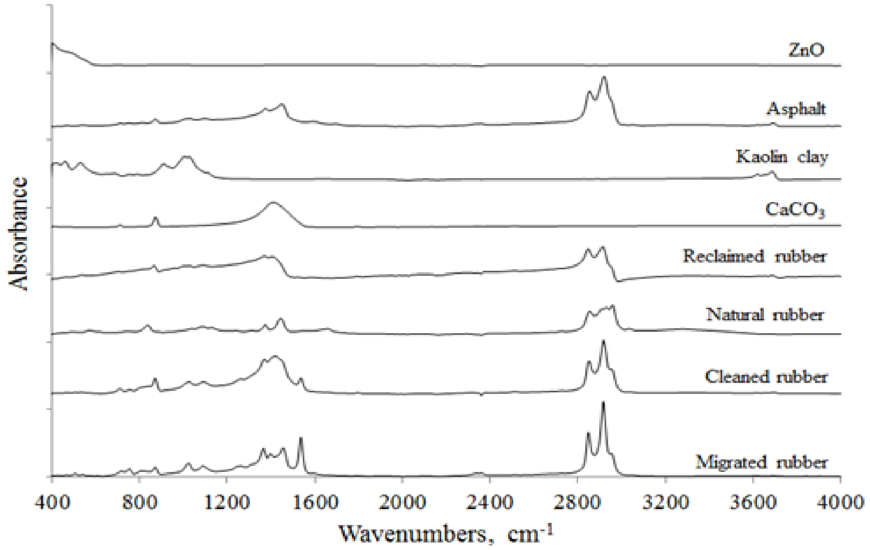

Figure 12. ATR-FTIR spectra of sample migrated and cleaned rubber specimen, raw natural rubber, and compounding ingredients 1-5.

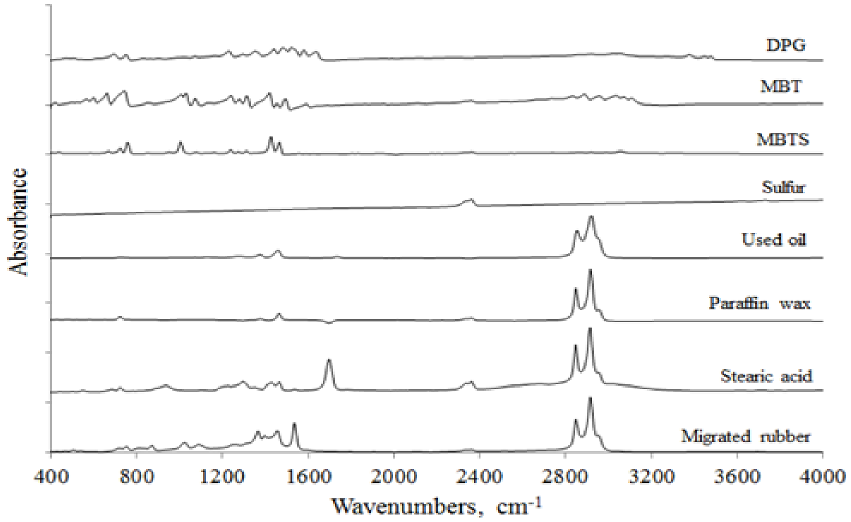

Figure 13. ATR-FTIR spectra of sample migrated and cleaned rubber specimen, raw natural rubber, and compounding ingredients 6-12.

Figures 14 – 16 illustrate the actual additive blooming and bleeding in the rubber sheet specimens due to surface migration of additives. In rubber compounds with low band intensity at 2800 cm^{-1} – 3000 cm^{-1}, small (white spots in Figure 14) and large (Figure 15) precipitates of migrated additives bloomed at the rubber surface. In Figure 16, used oil was shown bleeding from rubber sheet specimens of compound 12, forming semi-transparent wet patches at the rubber surface. Additive bleeding was mostly observed on rubber compounds with high absorption bands at 2800 cm^{-1} – 3000 cm^{-1}.

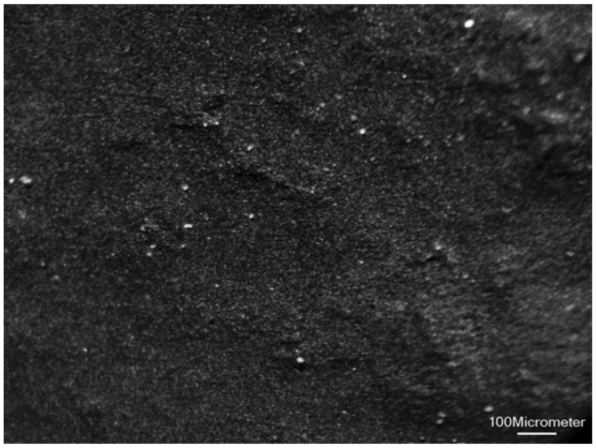

Figure 14. Additive blooming in compound 14 at ambient conditions.

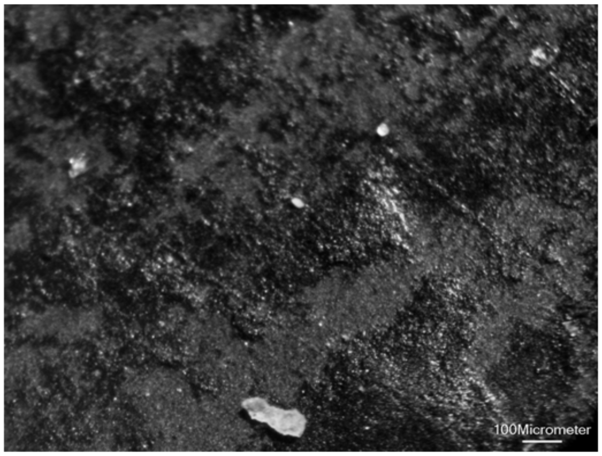

Figure 15. Additive blooming in compound 16 at ambient conditions.

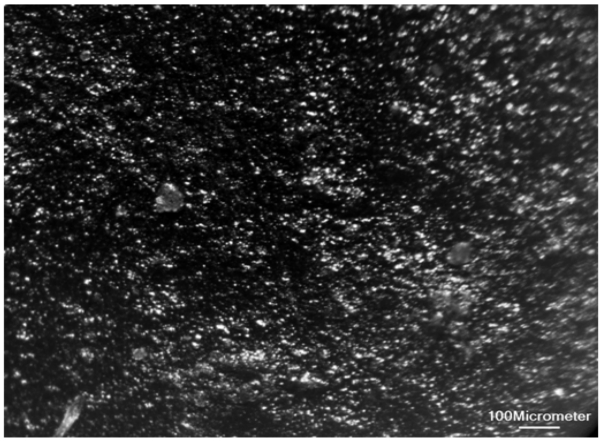

Figure 16. Additive bleeding in compound 12 at ambient conditions.

CONCLUSIONS

Loading of ingredients in formulations of natural rubber compounds has a significant effect on the surface migration kinetics of chemical additives at ambient conditions. In the studied formulation, increased loading of soluble ingredients such as used oil, stearic acid, and MBTS promoted blooming and bleeding in rubber sheets. High loading of asphalt in the formulation resulted in pseudo bloom due to surface degradation. In reducing overall migration of additives at the rubber surface, increased loading of other soluble ingredients such as sulfur and DPG was found to be effective. Wax, although a migrating additive, is observed to hinder the migration of other additives at increased loading. Non-soluble and non-migrating ingredients such as $CaCO_3$ lowered additive migration by increasing the diffusion path length within the rubber matrix. High loading of reclaimed rubber decreased blooming and bleeding by absorbing and retaining the migrating additives in the bulk.

ACKNOWLEDGMENTS

The authors acknowledge the Office of the Chancellor of the University of the Philippines Diliman, through the Office of the Vice-Chancellor for Research and Development, for funding support through the Ph.D. Incentive Awards (Project No. 131309 PhDIA). The authors also express their gratitude to Rhodora dela Cruz-Medalla of Rhodeco Rubber Processing Services, Inc. for compounding and vulcanization of rubber sheets.

REFERENCES

Auerbach I., Gehman S.D. 1954. Tracer Method for sulfur solubility and diffusivity in rubber. Anal Chem. 26(4): 685-690.

Bart J.C. 2006. Polymer additive analytics: industrial practice and case studies. Universita degli Studi di Firenze, Firenze University Press, Borgo Albizi, 28-50122 Firenze, Italy.

Basak G.C., Bandyopadhyay A., Bharadwaj Y.K., Sabharwal S., Bhowmick A.K.2010. Characterization of EPDM vulcanizates modified with gamma irradiation and trichloroisocyanuric acid and their adhesion behavior with natural rubber. J Adhesion. 86(3): 306-334.

Bielinski D., Glab P., Slusarski L. 2005. Surface segregation of carboxylic acids in styrene-butadiene rubber—effect of the bloom on friction. Compos Interface. 12(5): 445-457.

Choi S.S. 1997. Migration of antidegradants to the surface in NR and SBR vulcanizates. J Appl Polym Sci. 65(1): 117-125.

Choi S.S. 1998. Influence of silica content on migration of antidegradants to the surface in NR vulcanizates. J Appl Polym Sci. 68(11): 1821-1828.

Choi S.S. 1999. Migration behaviors of wax to surface in rubber vulcanizates. J Appl Polym Sci. 73(13): 2587-2593.

Choi S.S. 1999. Migration behaviors of antiozonants in binary rubberbased vulcanizates of NR, SBR, and BR. J Appl Polym Sci. 74(13): 3130-3136.

Choi S.S. 1999. Migration behaviors of antiozonants to the surface in NR vulcanizates, depending on the season: The effect of wax. J Appl Polym Sci. 71(12): 1987-1993.

Ciesielski A. 1999. An introduction to rubber technology. Shropshine: Rapra Technology Limited 189 p.

Dick J.S. 2009. Rubber technology: compounding and testing for performance. Munich: Carl Hanser Verlag.

Dick J.S. 2014. How to improve rubber compounds: 1800 experimental ideas for problem solving. Munich: Carl Hanser Verlag.

Jurkowski B., Jurkowska B. 1998. On the mechanism of sulfur behavior in rubber compounds. J Macromol Sci Phys. 37(2): 135-142.

Keen F.E., Lehrle R.S., Jakab E., Szekely T. 1992. The development of controlled-release antioxidants: A successful system demonstrated by its effect on the stabilisation of rubber. Polym Degrad Stabil. 38(3): 219-227.

Lazic Z.R. 2004. Design of experiments in chemical engineering. Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA.

Mark J.E., Erman B., Eirich F.R. 2005. Science and technology of rubber. USA: Elsevier Academic Press.

Nah S.H., Thomas A.G. 1980. Migration and blooming of waxes to the surface of rubber vulcanizates. J Polym Sci Pol Phys. 18(3): 511-521.

Parra D.F., Freire M.T.D.A., De Paoli M.A. 2000. Diffusion of amine stabilizers in vulcanized natural rubber compositions used in tires. J Appl Polym Sci. 75(5): 670-676.

Petersen J.C. 2009. A review of the fundamentals of asphalt oxidation: chemical, physicochemical, physical property, and durability relationships. Transportation Research E-Circular, (E-C140). Transportation Research Board, Washington, D.C.

Saeed F., Ansarifar A., Ellis R.J., Haile Meskel Y., Farid A.S. 2011. Effect of the blooming of chemical curatives on the cyclic fatigue life of natural rubber filled with a silanized silica nanofiller. J Appl Polym Sci. 120(5): 2497-2507.

Saeed F., Ansarifar A., Ellis R.J., Haile Meskel Y. 2012. Measuring effect of the blooming of chemical curatives on the rate of cyclic fatigue crack growth in natural rubber filled with a silanized silica nanofiller. J Appl Polym Sci. 124(2): 1372-1383.

Saeed F., Ansarifar A., Ellis R.J., Haile Meskel Y. 2012. Assessing effect of the reagglomeration and migration of chemical curatives on the mechanical properties of natural rubber vulcanizate. Adv Polym Tech. 32(S1): E153-165.

Sugiura M., Horii M., Hayashi H., Sasayama M. 1996. Application of sepiolite to prevent bleeding and blooming for EPDM rubber composition. Appl Clay Sci. 11(2): 89-97.

Torregrosa-Coque R., Alvarez-Garcia S., Martín-Martinez J.M. 2011. Migration of low molecular weight moiety at rubber–polyurethane interface: An ATR-IR spectroscopy study. Int J Adhes Adhes. 31(6): 389-397.

Torregrosa-Coque R., Alvarez-Garcia S., Martin-Martinez J.M. 2011. Effect of temperature on the extent of migration of low molecular weight moieties to rubber surface. Int J Adhes Adhes. 31(1): 20-28.

Venable C.S., Greene C.D. 1922. Solubility of sulfur in rubber. Ind Eng Chem. 14(4): 319-320.

Wake W.C., Tidd B.K., Loadman M.J.R. 1983. Analysis of rubber and rubber-like polymers. London: Applied Science.

Bryan B. Pajarito, D.Eng <bryan.pajarito@gmail.com> is an Assistant Professor at the Department of Chemical Engineering, University of the Philippines Diliman.

Christian Angeline de Torres and **Marienne Maningding** are B.S. Chemical Engineering graduate of the University of the Philippines Diliman.