

## **Effect of Zeolite Treatment on the Blooming Behavior of Paraffin Wax in Natural Rubber Composites**

**Bryan B. Pajarito\***

University of the Philippines Diliman

**Nico V. Berba**

University of the Philippines Diliman

**Jadreign Keisheen C. Parto**

University of the Philippines Diliman

**Raechel Anne V. Yabut**

University of the Philippines Diliman

### **ABSTRACT**

The blooming behavior of paraffin wax in natural rubber (NR) composites was studied as function of zeolite treatment. Three types of zeolite treatment were treated as factors: acid activation using hydrochloric acid (HCl) solution, ion exchange using tetradecyldimethyl amine (TDA) chloride salt, and organic modification using glycerol monostearate (GMS). The zeolite was treated according to a  $2^3$  full factorial design of experiment. Attenuated total reflectance – Fourier transform infrared (ATR-FTIR) spectroscopy was used to characterize the chemical structure of treated zeolite. Treated zeolite was applied as filler to NR composites deliberately compounded with high amount of paraffin wax. The amount of bloomed wax in surface of NR composite sheets was monitored with time at 50°C. Results show the bloom amount to be linear with the square root of time. NR composites reinforced with untreated, acid-activated, and ion-exchanged zeolite fillers indicate reduction in wax blooming as compared to unfilled NR. The bloom rate (slope) and initial bloom (y-intercept) were determined from the experimental plots. Analysis of variance (ANOVA) shows the bloom rate to be significantly increased when zeolite fillers are treated with GMS. Meanwhile, initial bloom was significantly enhanced when zeolite fillers are treated with TDA chloride

---

\*Corresponding Author

salt and GMS. The significant increase in bloom rate and initial bloom can be attributed to the softening of the NR matrix at high amounts of TDA chloride salt and GMS.

*Keywords:* Natural rubber, composite, paraffin wax, blooming, zeolite

## INTRODUCTION

Blooming is a phenomenon wherein soluble and oversaturated additives migrate from the bulk matrix and form a deposit at the rubber surface. The deposit can be solid precipitates or exudates of the migrated additives. A large number of additives are known to bloom in vulcanized rubber, such as sulfur, activators, antidegradants, various accelerators, process oils, and plasticizers (Venable and Greene 1922; Auerbach and Gehman 1954; Nah and Thomas 1980; Wake et al. 1983; Keen et al. 1992; Sugiura et al. 1996; Choi 1997, 1998, 1999a, 1999b; Jurkowski and Jurkowska 1998; Ciesielski 1999; Parra et al. 2000; Bielinski et al. 2005; Mark et al. 2005; Bart 2006; Dick 2009, 2014; Basak et al. 2010; Saeed et al. 2011, 2012a, 2012b; Torregrossa-Coque et al. 2011a, 2011b; ). While antidegradants, such as wax and paraphenylenediamines, are designed to purposely migrate at the rubber surface and create a passive barrier against ozone attack, the appearance of bloom is usually undesirable. Unwanted bloom can cause unaesthetic appeal, decreased building tack and interfered adhesion to material surfaces, skin irritation (Bart 2006), and reduced fatigue life of rubber (Saeed et al. 2011). It also increases manufacturing cost and lowers labor productivity. Bloomed surfaces of rejected rubber articles are usually washed with solvents or flushed with a steam jet (Pedretti 1967) for possible recycle or reuse. However, most cases of blooming are persistent and require further surface treatments.

Research works on additives that can reduce blooming in rubber are very few. Pedretti (1967) claimed additives from a group consisting of dialcohols, such as alkylene glycols and polyalkylene oxides; aliphatic polyalcohols, such as glycerine and erythrite; and mixtures of aliphatic alcohols in equal parts by weight with silicic acids, alkylene glycols, and polyalkylene oxides, as additives capable of lowering and inhibiting bloom. Sugiura et al. (1996) worked on the use of sepiolite on preventing bloom in ethylene-propylene-non-conjugated diene terpolymer (EPDM). Fujiki and Tanaka (2002) patented a bloom inhibitor, which comprises an alkylene oxide adduct of a saponified ethylene-saturated carboxylic acid vinyl ester copolymer and polyether compound.

This work employed zeolites as potential additives for reducing and inhibiting bloom in rubber. Zeolites are compounds of naturally occurring aluminosilicate minerals with symmetrically stacked alumina and silica tetrahedral, resulting to an open and stable three-dimensional crystalline structure (similar to a honeycomb) with a negative charge. They are often used as adsorbent and ion-exchange materials (Siriyong and Keawwattanna 2012). While inclusion of zeolite in rubber may yield to bloom reduction, its application does not always result to improved mechanical properties (Al-Ghamdi and Mark 1988; Siriyong and Keawwattanna 2012) due to its inherent hydrophilic nature and poor dispersion in the rubber matrix. Chemical treatments, such as acid activation, (Christidis et al. 2003; Bukit and Frida 2013), ion exchange with amine salts containing hydrophobic functional groups (Chakraborty et al. 2009), and organic modification with surfactants (Das et al. 2011; Rooj et al. 2012), can improve the compatibility of zeolite with rubber molecules. These treatments for inorganic mineral fillers are often cited for improving the physical and material properties of rubber composites; however, their effect on blooming behavior is yet to be explored.

This work studies the effect of different zeolite treatments on the blooming behavior of paraffin wax in natural rubber (NR) composites. Paraffin wax was chosen as a model compound to deliberately bloom in NR and its composites. Specifically, this work has the following objectives: (1) investigate the blooming behavior of paraffin wax with time; (2) determine the effect of reinforcing NR with raw and treated zeolite fillers to blooming behavior; and (3) determine how chemical treatment of raw zeolite affects blooming in NR composites. Three chemical treatments of raw zeolite were considered as factors in a full factorial design of experiment: acid activation using hydrochloric acid (HCl) solution, ion exchange using a tertiary amine chloride salt, and organic modification using a non-ionic surfactant. Attenuated total reflection – Fourier transform infrared (ATR-FTIR) spectroscopy was used to characterize the chemical structure of treated zeolite fillers. Amount of bloom in surface of rubber sheet specimens was monitored gravimetrically with time. From the experimental results, analysis of variance (ANOVA) was utilized to determine the zeolite treatments that have significant effects on the blooming behavior. Main and interaction effects of significant zeolite treatments were computed and discussed.

## MATERIALS AND METHODS

### Materials

Zeolite powder (HSCAS, Saile Industries) was used as received. The untreated powder has a cation exchange capacity (CEC) of 171.55 meq per 100 g of zeolite. HCl (AR1107-G2.5L, RCI Labscan Limited) was used for the acid activation of zeolite. Tetradecyldimethylamine TDA (FARMIN D4098, Pilipinas Kao, Inc.) and glycerol monostearate GMS (Cerin GMS 100 SE, Chemrez Technologies, Inc.) were utilized for ion exchange and organic modification of zeolite, respectively. Figure 1 shows the chemical structures of TDA and GMS.

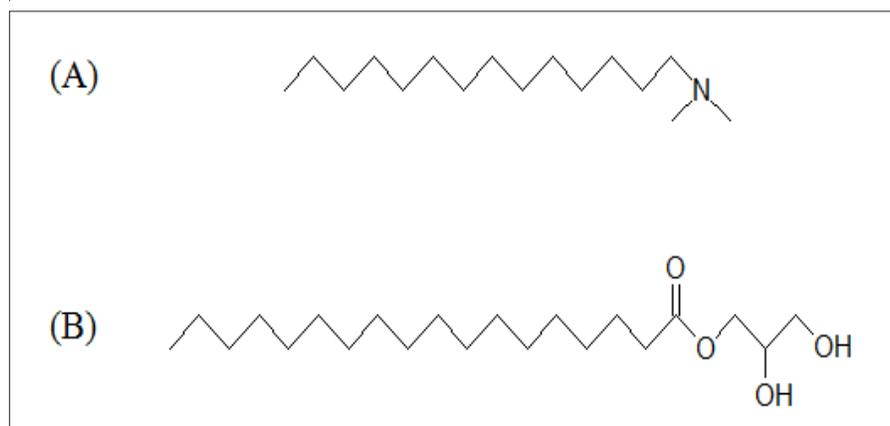


Figure 1. Chemical structures of (A) TDA and (B) GMS.

### Acid Activation

Two liters of HCl solution at specified concentration (1.5 or 3 M) were prepared in a 4-liter glass beaker at 80°C. Zeolite (166.7 g) was added to the hot solution and stirred occasionally for 40 minutes. After stirring, the hot slurry was cooled at room temperature, allowing zeolite to settle at the bottom of the beaker. Excess liquid was filtered using a Buchner setup to recover acid-activated zeolite. After filtration and decantation, acid-activated zeolite was washed with tap water until the pH of wash water is greater than six. Treated zeolite was then recovered by filtration and oven dried at 95°C for at least 24 hours. Dried acid-activated zeolite was further ground using a mortar and pestle before storage in a sealed plastic container.

### Ion Exchange with Amine Salt

Sixty grams of zeolite was dispersed in three liters of distilled water in a 4-liter beaker using a disperser (IKA T50 Digital ULTRA-TURRAX) for one minute at 5000 rpm. Mixing temperature was maintained at 80°C using a silicone rubber heating tape (BriskHeat) controlled by a digital thermostat (DT-6, UPLift Accessories). A required amount of TDA (1.5 or 3 equivalent times the CEC of zeolite) was stirred with an equivalent amount of HCl solution in 500 mL water at 80°C. The hot amine salt solution was then added to the zeolite slurry, with the stirring continuing for an hour at 80°C and 1250 rpm using a digital overhead stirrer (IKA RW20). After stirring, the hot slurry was cooled at room temperature. Ion-exchanged zeolite was recovered by sedimentation, decantation, and Buchner filtration. The collected zeolite was oven dried at 95°C and ground with mortar and pestle before storage.

### Organic Modification with Surfactant

One hundred twenty grams of zeolite was mixed with specified amounts of GMS (1.5 or 3 wt% of zeolite) using mortar and pestle. The mortar, along with the mixture, was kept in an oven at 100°C for 15 minutes. The mixture was then homogenized thoroughly at hot condition with the pestle. The process was repeated three times before storage.

### Design of Experiment

Table 1 shows the 2<sup>3</sup> full factorial design (Lazic 2004) employed during the chemical treatment and preparation of zeolite fillers. Sample l is the raw and untreated

**Table 1. Full factorial design of experiment employed during chemical treatment and preparation of zeolite fillers**

Label	A-HCl Concentration, M	B-Amount of TDA salt, nX the CEC of zeolite	C-Amount of GMS, wt% of zeolite
l	0	0	0
a	3	0	0
b	0	3	0
c	0	0	3
ab	3	3	0
ac	3	0	3
bc	0	3	3
abc	3	3	3
0	1.5	1.5	1.5

zeolite, while samples a, b, and c are the acid-activated (3 M of HCl solution), ion-exchanged (TDA chloride salt at 3X the CEC of zeolite), and organo-modified (GMS at 3 wt% of zeolite) zeolites, respectively. Zeolites from varied combinations of treatments (samples ab, ac, bc, and abc) were also prepared as required by the design of experiment. Sample 0 was treated with 1.5 M of HCl solution, TDA chloride salt at 1.5X the CEC of zeolite, and GMS at 1.5 wt% of zeolite. A total of nine samples of zeolite fillers (95 g each sample) were prepared and oven dried at 120°C for at least 48 hours before sending to Rhodoco Rubber Processing Services, Inc. (Caloocan City) for the compounding and vulcanization of the NR composites.

### **ATR-FTIR Spectroscopy of Treated Zeolite**

Chemical changes on the treated zeolite samples were studied using an FTIR spectrometer (Thermo Nicolet 6700) coupled with a macro diamond ATR crystal plate accessory. A total of 32 scans were co-added at 2 cm<sup>-1</sup> resolution from mid-infrared range of 400 to 4000 cm<sup>-1</sup>. Background spectra were obtained without zeolite samples prior to actual analysis.

### **NR Composite Formulation**

Table 2 shows the formulation of the NR composite used during compounding. The formulation was derived from previous work (Pajarito et al. 2014) with additives, such as reclaimed rubber, calcium carbonate (CaCO<sub>3</sub>), kaolin clay, asphalt, and used oil, replaced by zeolite filler. Moreover, the amount of paraffin wax in the formulation was deliberately increased from 1.50 to 7.50 phr to induce blooming. Natural rubber and zeolite filler were first mixed in a two roll mill, followed by zinc oxide, stearic acid, and paraffin wax. The resulting master batch was aged for 24 hours at ambient conditions before roll milling again with sulfur, mercaptobenzothiazole disulfide (MBTS), mercaptobenzothiazole (MBT), and diphenylguanidine (DPG). NR composites were vulcanized using a heated compression moulding press at 160°C for 20 minutes. Rubber sheets have final dimensions of 300 x 300 x 3 mm. It should be noted that all NR specimens (unfilled NR and 9 types of NR composites) were compounded for two days before being subjected to vulcanization (~ 0.5 day). All vulcanized NR sheets were cooled at ambient conditions for at least an hour, packed, and delivered to Polymer Research Laboratory for testing. Accelerated blooming experiment was immediately performed after receipt of NR sheets.

**Table 2. Formulation of NR composite used during compounding**

Ingredient	phr
Natural rubber (SPR 20)	100.00
Zinc oxide	6.00
Stearic acid	1.50
Sulfur	2.50
Mercaptobenzothiazole disulfide (MBTS)	1.50
Mercaptobenzothiazole (MBT)	1.50
Diphenylguanidine (DPG)	1.50
Paraffin wax	7.50
Zeolite filler	4.75

### Accelerated Blooming Experiment

Specimens of 50 x 50 mm were cut from the NR composite sheets. Initial weights of the specimens ( $W_i$ ) were recorded before the experiment. The blooming experiment was performed using a laboratory oven maintained at 50°C for 120 hours. Specimens were stored in individual aluminium foil pouches before they were placed in the oven. The amount of bloom was determined by periodically removing the bloomed additives from the rubber surface using five passes of adhesive tape (Scotch tape), and measuring the resulting weight loss in an analytical balance (Nah and Thomas 1980). Bloom amount ( $M_t$  in wt%) in rubber specimens was calculated by:

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

where  $W_t$  is the weight of specimen after bloom removal using adhesive tape at time  $t$ . Three replicate NR composite specimens per zeolite sample were used to report the average bloom amount.

### RESULTS AND DISCUSSION

Figure 2a shows the ATR-FTIR spectra of the zeolite samples. All spectra show distinct peaks at 439 – 447  $\text{cm}^{-1}$  and 1018 – 1034  $\text{cm}^{-1}$ , indicating Si-O or Al-O bending mode and asymmetric tetrahedral stretching, respectively (Christidis et al. 2003). Decrease in the intensity and broadening of peak at 1018 – 1034  $\text{cm}^{-1}$  for

acid-activated zeolite samples indicate the destruction of free linkages and Si-tetrahedra by dealumination. Dealumination by acid activation is also indicated by the slight shift of peak at 1018 – 1034  $\text{cm}^{-1}$  to higher wave numbers (Holmberg et al. 2004).

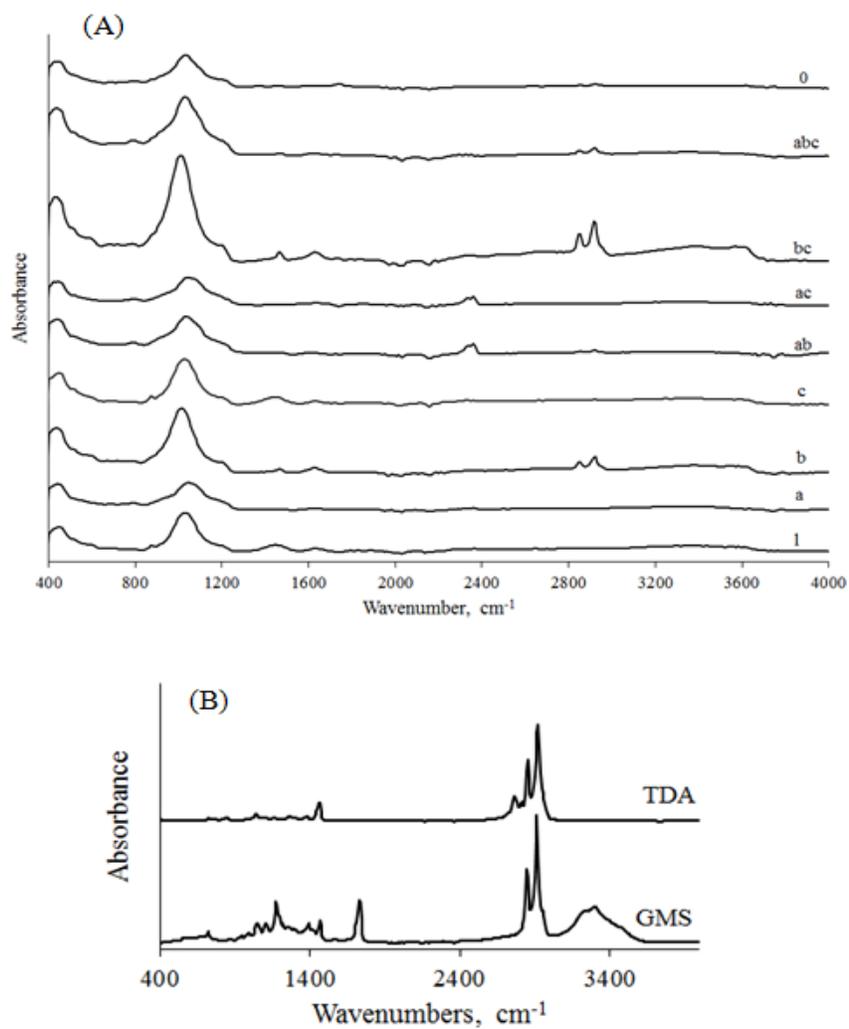


Figure 2. ATR-FTIR spectra of (A) zeolite samples and (B) TDA and GMS.

Zeolite samples ion exchanged with TDA chloride salt display specific peaks at 1427 – 1460, 2846 – 2854, and 2916 – 2924  $\text{cm}^{-1}$ . The peaks at 2846 – 2854 and 2916 – 2924  $\text{cm}^{-1}$  are prominent in samples b and bc, partially visible in sample abc, and faint in sample 0. A small peak at 1427 – 1460  $\text{cm}^{-1}$  is also observed in samples b, bc, and abc. These peaks can also be found in the ATR-FTIR spectrum of TDA (Figure 2b), which can be attributed to C-H, C-C, and N-C vibrations in the tertiary amine salt (Nezamzadeh-Ejhi and Badri 2011).

Zeolite samples organo-modified with GMS (samples c, ac, bc, abc, and 0) do not exhibit the broad O-H peak at 3300  $\text{cm}^{-1}$  and the C=O stretch at 1735  $\text{cm}^{-1}$  for carbonyls, carboxylic, and its derivatives, which are functional groups present in GMS (Figures 1 and 2b). This result is expected due to the small amount of GMS used during organic modification (1.5 or 3 wt% of zeolite).

It should be noted that the chemical treatments also change the particle size of zeolite fillers. For instance, raw and untreated zeolite has a median diameter (measured by sieve analysis) of 52.9  $\mu\text{m}$ . Acid activation decreases the measured particle size (e.g. median diameter of sample a is 37.5  $\mu\text{m}$ ), while ion exchange with TDA chloride salt and organic modification with GMS increase the particle size (e.g. median diameter of sample bc is 78.3  $\mu\text{m}$ ). The decrease in particle size after acid activation is due to dealumination, while the increase in particle size after ion exchange and organic modification can be attributed to the aggregation of treated zeolite fillers. It is noticeable during preparation that the acid-activated zeolite fillers are visually finer than raw zeolite, while ion-exchanged and GMS-treated zeolite fillers are sticky and tend to form clumps during drying.

Figure 3a shows an optical image of NR composite surface covered with bloomed paraffin wax. Bloomed paraffin wax was removed and collected from the rubber surface using adhesive tape (Figure 3b). The resulting weight loss is equivalent to bloom amount. Figure 4 shows the bloom amount in terms of cumulative weight loss in NR composite specimens as a function of the square root of time at 50°C. All specimens show increasing bloom amount with time. As predicted by Nah and Thomas (1980), bloom amount was also found to be linear with the square root of time, which indicates diffusion by Fickian mechanism. The experimental plots have non-zero bloom amount at  $t = 0$  h, indicating the presence of wax bloom at the specimen surface even before the blooming experiment was initiated. NR composites reinforced with raw (sample l), acid-activated (sample a), ion-exchanged (sample b), and both acid-activated and ion-exchanged (sample ab) zeolite fillers exhibit decrease in wax blooming as compared to NR without zeolite. In terms of

reducing bloom in NR composites, the zeolite fillers can be ranked as follows:  $l > a > ab > b$ . The observed reduction in blooming due to the inclusion of zeolite in NR can be attributed to the inherent porosity of the fillers. Meanwhile, zeolite sample c has the same blooming behavior as NR without zeolite (Figure 4a), while samples ac, bc, abc, and 0 enhance wax blooming (Figure 4b). Zeolite ac has the highest bloom amount among the samples ( $ac > bc > 0 > abc > c$ ). While zeolite fillers are expected to impart rigidity in the rubber matrix and impede the migration of paraffin wax to the rubber surface, the treatment with GMS could have lowered the inherent porosity of natural zeolite, with GMS molecules occupying and limiting

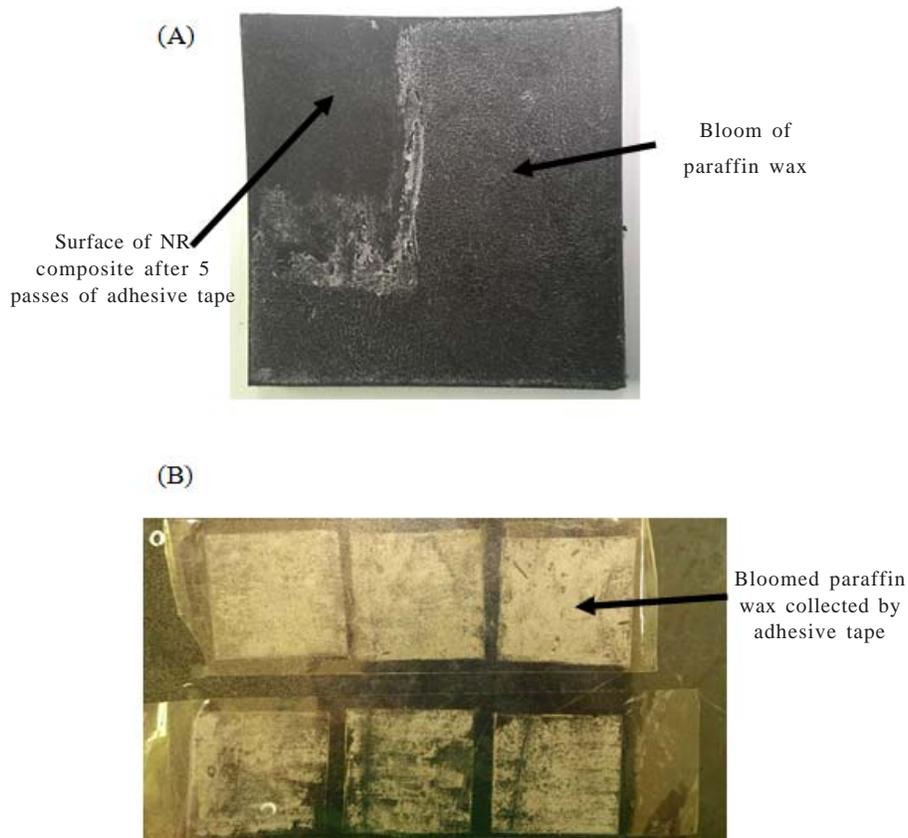


Figure 3. Optical images of (A) NR composite surface covered with bloomed paraffin wax, and (B) bloomed paraffin wax removed and collected from the rubber surface using adhesive tape.

the availability of the pores for wax adsorption. Unreacted GMS (molecules of GMS not attached to zeolite) could also have plasticized the rubber matrix, negating the rigidity offered by zeolite fillers and allowing paraffin wax to diffuse through the soft rubber matrix. Note that combining GMS treatment with acid activation (samples ac, 0, and abc) and ion exchange with TDA salt (samples bc, 0, and abc) result to an increase in bloom amount when compared to NR without zeolite and NR filled with sample zeolite c. The reduction in bloom amount observed in NR containing zeolite samples a, b, and ab can be considered ineffective after the addition of the GMS treatment. The effect of GMS treatment on bloom amount is more pronounced as compared to other zeolite treatments.

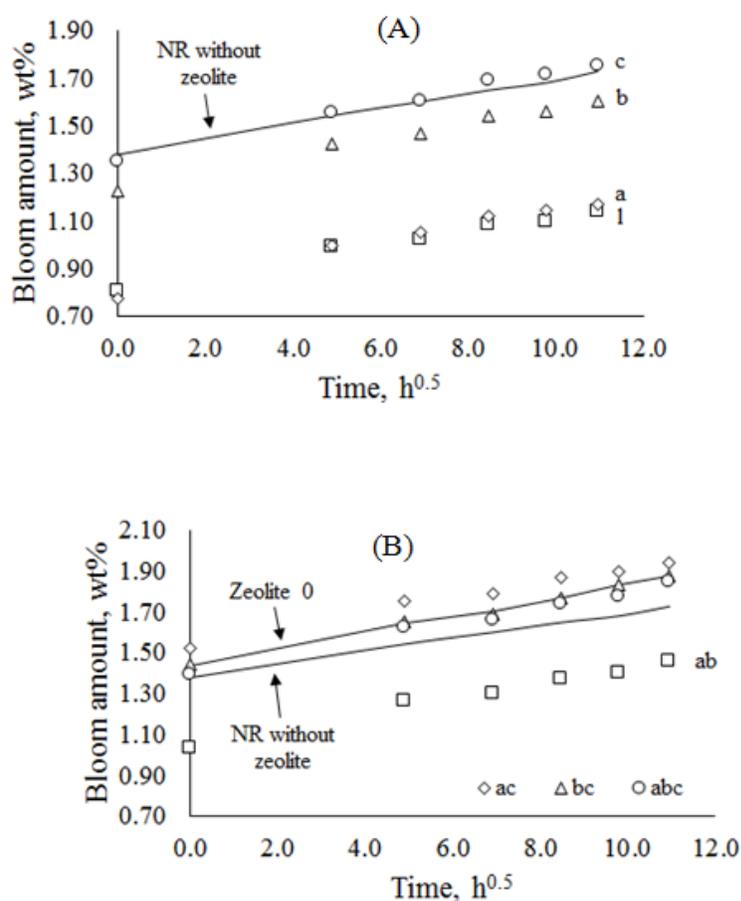


Figure 4. Bloom amount in terms of cumulative weight loss in NR composite specimens as function of the square root of time at 50°C.

A line was fitted with the experimental data to determine the bloom rate (slope of the line in  $\% \cdot h^{-0.5}$ ) and initial bloom ( $y$ -intercept in %). Table 3 shows the average bloom rate and initial bloom determined from the experimental plots. The coefficient of determination  $r^2$  calculated from 30 data sets (8 samples from  $2^3$  full factorial design, sample 0, and control; 3 replicates each zeolite sample) ranges from 0.952 to 0.999. In terms of bloom rate, raw zeolite (sample l) shows the lowest value at  $0.030 \% \cdot h^{-0.5}$ , while zeolite activated with 1.5 M HCl, ion exchanged with TDA chloride salt at 1.5X the CEC of zeolite, and organo-modified with GMS at 1.5 wt% of zeolite (sample 0) yields the highest value at  $0.040 \% \cdot h^{-0.5}$ . For the initial bloom, acid-activated zeolite (sample a) exhibits the lowest at 0.789%, while acid-activated and organo-modified zeolite (sample ac) shows the highest value at 1.537%.

**Table 3. Average bloom rate and initial bloom determined from the experimental plots**

Label	Bloom rate, $\% \cdot h^{-0.5}$	Initial bloom, %
l	0.030	0.816
a	0.036	0.789
b	0.034	1.232
c	0.037	1.354
ab	0.037	1.044
ac	0.037	1.537
bc	0.039	1.438
abc	0.039	1.400
0	0.040	1.434
NR without zeolite	0.031	1.380

Using bloom rate and initial bloom as responses, ANOVA was executed in Minitab 17 to determine the significant main and interacting factor treatments affecting blooming behavior in NR composites. The following model was utilized during ANOVA:

$$y = \beta_0 + \beta_A X_A + \beta_B X_B + \beta_C X_C + \beta_{AB} X_A X_B + \beta_{AC} X_A X_C + \beta_{BC} X_B X_C + \beta_{ABC} X_A X_B X_C \quad (2)$$

where  $y$  is the response (bloom rate or initial bloom),  $\hat{\alpha}_0, \hat{\alpha}_A, \dots, \hat{\alpha}_C$  are the regression coefficients,  $X_A$  - is HCl concentration during acid activation (0 or 3 M),  $X_B$  - is amount of TDA chloride salt ( $nX$  the CEC of zeolite) during ion exchange (0 or 3), and  $X_C$  is the amount of GMS during organic modification (0 or 3 wt% of zeolite). After data analysis, response functions obtained for the bloom rate ( $y_1$ ) and initial bloom ( $y_2$ ) are given by Equations 3 and 4, respectively:

$$y_1 = 0.0298 + 0.0022X_A + 0.0015X_B + 0.0024X_C - 0.0004X_A X_B - 0.0007X_A X_C - 0.0003X_B X_C + 0.0001X_A X_B X_C \quad (3)$$

$$y_2 = 0.8157 - 0.0088X_A + 0.1386X_B + 0.1793X_C - 0.0179X_A X_B + 0.0233X_A X_C - 0.0368X_B X_C - 0.0022X_A X_B X_C \quad (4)$$

Tables 4 and 5 show the ANOVA results for bloom rate and initial bloom, respectively. For bloom rate, only the organic modification using GMS was found to be statistically significant at 95% confidence level ( $p = 0.035$ ). Figure 5 shows the main effect of acid activation (A), ion exchange with TDA chloride salt (B), and organic modification with GMS (C) on bloom rate of NR composites reinforced with zeolite. The treatment with GMS surfactant at 3 wt% of zeolite significantly increased the bloom rate from 0.034 to 0.038 %-h<sup>-0.5</sup>. Though not statistically significant, acid activation and ion exchange with TDA chloride salt are also observed to increase bloom rate in NR composites.

In the case of the initial bloom, the main and interaction effects of ion exchange with TDA chloride salt and organic modification with GMS are found to be statistically significant. Figure 6 shows the main effect of acid activation (A), ion exchange with TDA chloride salt (B), and organic modification with GMS (C) on initial bloom of NR composites reinforced with zeolite. Ion exchange treatment significantly increased the initial bloom from 1.124% to 1.279% ( $p = 0.028$ ). Organic modification with GMS has the same direction of effect, enhancing the initial bloom from 0.970% to 1.432% ( $p = 0.000$ ). In terms of magnitude, organic modification with GMS has higher effect on increasing the initial bloom than ion exchange with TDA chloride salt. While statistically insignificant, acid activation is observed to decrease the initial bloom from 1.210% to 1.193%.

Figure 7 shows the interaction effect of ion exchange with TDA chloride salt (B) and organic modification with GMS (C) on the initial bloom of NR composites reinforced with zeolite ( $p = 0.012$ ). The increase in initial bloom due to ion exchange from 0.802% to 1.138% is observed when zeolite is not organo-modified with GMS. However, the effect of ion exchange on initial bloom is severely diminished when zeolite is treated with GMS. The magnitude of increase in initial bloom due to organic modification with GMS is also reduced when zeolite is treated with TDA chloride salt.

**Table 4. ANOVA result for bloom rate**

Source	Degree of Freedom	Adjusted Sum of Squares	Adjusted Mean Squares	p value
Model	7	0.000197	0.000028	0.145
Linear	3	0.000157	0.000052	0.042
A – Acid activation	1	0.000040	0.000004	0.124
B – Ion exchange	1	0.000036	0.000036	0.142
C – GMS modification	1	0.000081	0.000081	0.035
2-Way Interactions	3	0.000036	0.000012	0.520
A*B	1	0.000006	0.000006	0.549
A*C	1	0.000030	0.000030	0.182
B*C	1	0.000001	0.000001	0.856
3-Way Interaction	1	0.000005	0.000005	0.587
A*B*C	1	0.000005	0.000005	0.587
Error	16	0.000243	0.000015	
Total	23	0.000440		

**Table 5. ANOVA result for initial bloom**

Source	Degree of Freedom	Adjusted Sum of Squares	Adjusted Mean Squares	p value
Model	7	1.72666	0.24667	0.000
Linear	3	1.42664	0.47555	0.000
A – Acid activation	1	0.00178	0.00178	0.791
B – Ion exchange	1	0.14383	0.14383	0.028
C – GMS modification	1	1.28102	1.28102	0.000
2-Way Interactions	3	0.29865	0.09955	0.025
A*B	1	0.05471	0.05471	0.154
A*C	1	0.04817	0.04817	0.180
B*C	1	0.19577	0.19577	0.012
3-Way Interaction	1	0.00137	0.00137	0.816
A*B*C	1	0.00137	0.00137	0.816
Error	16	0.39141	0.02446	
Total	23	2.11807		

The increase in bloom rate and initial bloom of paraffin wax in NR composites reinforced with zeolite can be attributed to the softening of the NR matrix. During chemical treatment of zeolite, TDA chloride salt and GMS are applied in excess to ensure complete exchange of inorganic cations and successful hydrophobization of zeolite surface. However, excess and unreacted TDA salt and GMS in treated zeolite filler can act as a lubricating or softening agent (Chakraborty et al. 2009). Plasticized NR matrix lowers the diffusion resistance for wax blooming. To check if chemical

treatments of zeolite filler result to NR matrix softening, Shore A hardness of composite specimens was measured. Computation of relative factor effects (Pajarito et al. 2014; Pajarito 2015; Pajarito and Arabit 2015) shows that the ion exchange treatment of zeolite filler reduces the hardness of the NR composites by 3.627% as compared to the untreated zeolite. Organic modification with GMS also lowers the hardness of NR composites by 4.982%.

The results of the ANOVA and Figure 7 suggest the synergistic effect between TDA chloride salt and GMS in reducing initial bloom in NR composites. The addition of GMS after ion exchange treatment of zeolite filler with TDA chloride salt increases the concentration of long  $\text{CH}_2$  moieties in the NR matrix. Other than solubilizing and plasticizing the NR matrix, these functional groups can also interact with paraffin wax and reduce its migration due to affinity in chemical structure. The observed decrease in magnitude of factor effects to initial bloom after combining ion exchange and organic modification treatments can be attributed to this interaction.

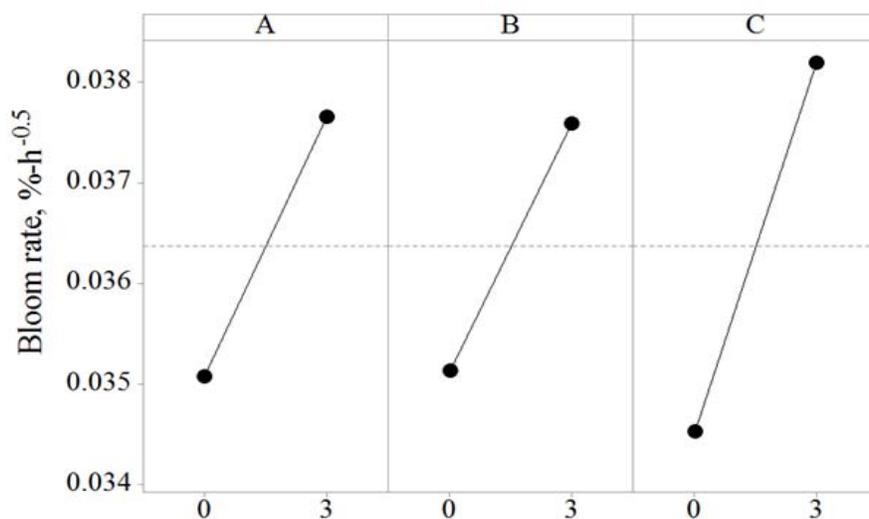


Figure 5. Main effect of (A) acid activation, (B) ion exchange with TDA chloride salt, and (C) organic modification with GMS on the bloom rate of NR composites reinforced with zeolite.

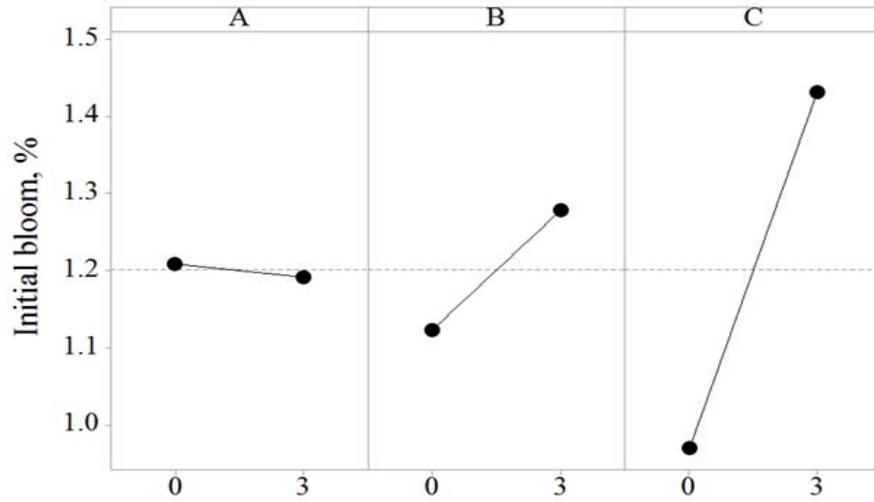


Figure 6. Main effect of (A) acid activation, (B) ion exchange with TDA chloride salt, and (C) organic modification with GMS on the initial bloom of NR composites reinforced with zeolite.

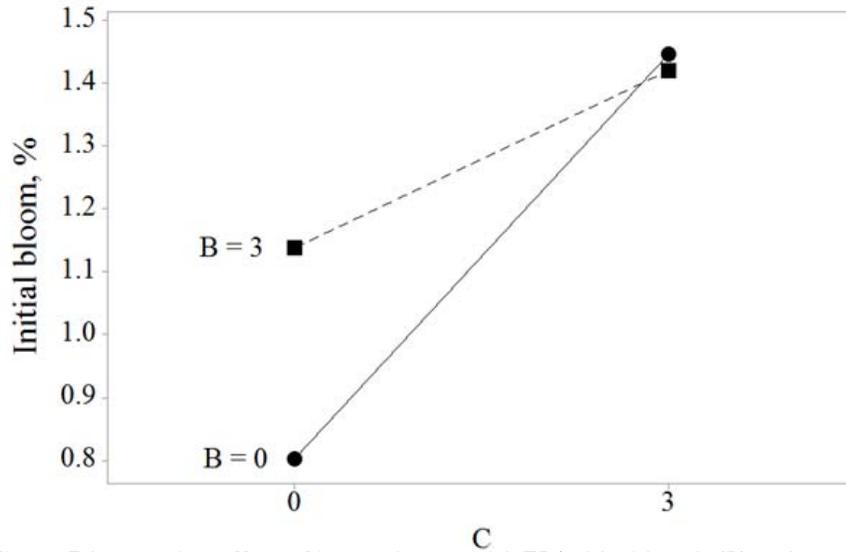


Figure 7. Interaction effect of ion exchange with TDA chloride salt (B) and organic modification with GMS (C) on the initial bloom of NR composites reinforced with zeolite.

## CONCLUSIONS

The amount of paraffin wax blooming at the surface of unfilled NR and NR composites reinforced with raw and treated zeolite fillers varies linearly with the square root of time. This behavior suggests the Fickian diffusion of paraffin wax in the NR matrix. Reinforcing NR with raw, acid-activated, ion-exchanged with TDA chloride salt, and both acid-activated and ion-exchanged zeolite fillers reduces the amount of paraffin wax blooming in NR. Raw and acid-activated zeolites are the most effective in decreasing the amount of bloom. Meanwhile, the amount of bloomed wax is increased when NR is reinforced with GMS-treated zeolite fillers. Among the chemical treatments, organic modification of raw zeolite with GMS significantly increases the bloom rate and initial amount of bloom in NR composites. Zeolite treatment by ion exchange with TDA chloride salt also enhances initial amount of bloom in NR composites.

## 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. 141417 PhDIA). The authors also express their gratitude to Rhodora dela Cruz – Medalla of Rhodoco Rubber Processing Services, Inc. for the compounding and vulcanization of rubber sheets.

## REFERENCES

- Al-Ghamdi AMS, Mark JE. 1988. Zeolites as reinforcing fillers in an elastomer. *Polym Bull.* 20(6):537-542.
- Auerbach I, Gehman SD. 1954. Tracer Method for sulfur solubility and diffusivity in rubber. *Anal Chem.* 26(4):685-690.
- Bart JC. 2006. *Polymer additive analytics: industrial practice and case studies.* Florence: Firenze University Press.
- Basak GC, Bandyopadhyay A, Bharadwaj YK, Sabharwal S, Bhowmick AK. 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.
- Bukit N, Frida E. 2013. The effect zeolite addition in natural rubber polypropylene composite on mechanical, structure, and thermal characteristics. *Makara Seri Teknologi*. 17(3):113-120.
- Chakraborty S, Sengupta R, Dasgupta S, Mukhopadhyay R, Bandyopadhyay S, Joshi M, Ameta SC. 2009. Synthesis and characterization of in situ sodium-activated and organomodified bentonite clay/styrene-butadiene rubber nanocomposites by a latex blending technique. *J Appl Polym Sci*. 113(2):1316-1329.
- Choi SS. 1997. Migration of antidegradants to the surface in NR and SBR vulcanizates. *J Appl Polym Sci*. 65(1):117-125.
- Choi SS. 1998. Influence of silica content on migration of antidegradants to the surface in NR vulcanizates. *J Appl Polym Sci*. 68(11):1821-1828.
- Choi SS. 1999. Migration behaviors of wax to surface in rubber vulcanizates. *J Appl Polym Sci*. 73(13):2587-2593.
- Choi SS. 1999. Migration behaviors of antiozonants in binary rubberbased vulcanizates of NR, SBR, and BR. *J Appl Polym Sci*. 74(13):3130-3136.
- Choi SS. 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.
- Christidis GE, Moraetis D, Keheyam E, Akhalbedashvili L, Kekelidze N, Gevorkyan R, Yeritsyan H, Sargsyan H. 2003. Chemical and thermal modification of natural HEU-type zeolitic materials from Armenia, Georgia and Greece. *Appl Clay Sci*. 24(1):79-91.
- Ciesielski A. 1999. An introduction to rubber technology. Shropshire: Rapra Technology Limited.
- Das A, Stockelhuber KW, Jurk R, Jehnichen D, Heinrich G. 2011. A general approach to rubber-montmorillonite nanocomposites: Intercalation of stearic acid. *Appl Clay Sci*. 51(1-2):117-125.
- Dick JS. 2009. Rubber technology: compounding and testing for performance. Munich: Carl Hanser Verlag.
- Dick JS. 2014. How to improve rubber compounds: 1800 experimental ideas for problem solving. Munich: Carl Hanser Verlag.
- Fujiki T, Tanaka M. 2002. Blooming preventing agent. U.S. Patent No. 6,433,080. Washington: U.S. Patent and Trademark Office.
- Holmberg BA, Wang H, Yan Y. 2004. High silica zeolite Y nanocrystals by dealumination and direct synthesis. *Micropor Mesopor Mat*. 74(1):189-198.

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

Keen FE, Lehrle RS, 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 ZR. 2004. Design of experiments in chemical engineering. Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA.

Mark JE, Erman B, Eirich FR. 2005. Science and technology of rubber. USA: Elsevier Academic Press.

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

Nezamzadeh-Ejhieh A, Badri A. 2011. Surfactant modified ZSM-5 zeolite as an active component of membrane electrode towards thiocyanate. *Desalination.* 281:248-256.

Pajarito BB, de Torres CA, Maningding M. 2014. Effect of ingredient loading on surface migration kinetics of additives in vulcanized natural rubber compounds. *Sci Diliman.* 26(2):21-39.

Pajarito B, Arabit J. 2015. Effect of ingredient loading on surface migration of additives in a surfactant-loaded natural rubber vulcanizate. *Adv Mat Res.* 1125:64-68.

Pajarito B. 2015. Effect of ingredient loading on vulcanization characteristics of a natural rubber compound. *Adv Mat Res.* 1125:50-54.

Parra DF, Freire MTDA, De Paoli MA. 2000. Diffusion of amine stabilizers in vulcanized natural rubber compositions used in tires. *J Appl Polym Sci.* 75(5):670-676.

Pedretti G. 1967. Vulcanizable compositions comprising olefinic polymers and vulcanizates obtained therefrom. U.S. Patent No. 3,317,454. Washington: U.S. Patent and Trademark Office.

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

Rooj S, Das A, Stockelhuber KW, Reuter U, Heinrich G. 2012. Highly exfoliated natural rubber/clay composites by "propping-open procedure": the influence of fatty-acid chain length on exfoliation. *Macromol Mater Eng.* 297(4):369-383.

Saeed F, Ansarifar A, Ellis RJ, HaileMeskel Y, Farid AS. 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 RJ, HaileMeskel 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 RJ, HaileMeskel Y. 2013. Assessing effect of the reagglomeration and migration of chemical curatives on the mechanical properties of natural rubber vulcanizate. *Adv Polym Tech.* 32(S1):E153-E165.

Siriyong T, Keawwattana W. 2012. Utilization of different curing systems and natural zeolite as filler and absorbent for natural rubber/nitrile rubber blend. *Kasetsart J Nat Sci.* 46(6):918-930.

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 JM. 2011. Migration of low molecular weight moiety at rubber-polyurethane interface: An ATR-IR spectroscopy study. *Int J Adhes.* 31(6):389-397.

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

Venable CS, Greene CD. 1922. Solubility of sulfur in rubber. *Ind Eng Chem.* 14(4):319-320.

Wake WC, Tidd BK, Loadman MJR. 1983. *Analysis of rubber and rubber-like polymers.* London: Applied Science.

---

**Bryan B Pajarito** <bryan.pajarito@gmail.com> is an associate professor and researcher at the Department of Chemical Engineering, University of the Philippines Diliman. He obtained his MEng and DEng in Chemical Engineering at Tokyo Institute of Technology (Japan). His current research interests involve optimizing formulations of oxo-biodegradable PE films for commercial use, developing clay fillers for rubber compounding, and investigating novel thermoset-based composites for barrier applications.

**Nico V. Berba, Jadreign Keisheen C. Parto, and Raechel Anne V. Yabut** were undergraduate research advisees of Dr. Pajarito under Polymer Research Laboratory, Department of Chemical Engineering, University of the Philippines Diliman.