STRUCTURAL AND THERMAL STABILIZATIONS OF PVC AND WOOD/PVC COMPOSITES BY METAL STEARATES AND ORGANOTIN☆

Kantima Chaochanchaikul,[a] Vichai Rosarpitak,[b] and Narongrit Sombatsompop [a*]

Structural and thermal stabilizations of poly(vinyl chloride) (PVC) and wood/PVC (WPVC) composites were studied using lead stearate ($PbSt_2$), calcium/zinc complex (Ca/Zn) stabilizers, and methyl tin mercaptide (MT). Thermal and structural stabilities of PVC and WPVC composites were assessed using FTIR spectrometer, thermogravimetric analysis (TGA) and UV-Vis spectrophotometry. The results indicated that the additions of thermal stabilizers into PVC and WPVC composites could promote the thermal stabilities under both un-aged and thermally aged conditions. The presence of wood particles resulted in increases in polyene and carbonyl sequences during processing and decreases in the decomposition temperature (T_d). The presence of wood was found to accelerate the thermal degradation in PVC, and suppressed the efficiencies of the thermal stabilizers used. By increasing the stabilizer dosage, the thermal degradations of PVC and WPVC were moderated. Under thermally aged condition at 177°C, the additions of thermal stabilizer could decrease the increase in yellowness index (*YI*) and discoloration at different ageing times. In this work, MT was found to be the most suitable and promising stabilizer for PVC and WPVC composites, considering the polyene and carbonyl contents, T_d, the shift of derivative thermogravimetric (DTG) curves, and changes in *YI* value and visual color.

Keywords: Poly(vinyl chloride); Wood flour; Thermal stabilizer; Composite; Extrusion

Contact information: a: School of Energy, Environment and Materials, King Mongkut's University of Technology Thonburi (KMUTT), 126 Pracha-u-tid Rd., Bangmod, Toongkru, Bangkok 10140, Thailand;
b: V.P. Wood Co., Ltd., 25/5 Moo 4, Soi Suksawad 66, Bangmod, Thungkru, Bangkok 10140, Thailand;
** Corresponding author: narongrit.som@kmutt.ac.th*

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INTRODUCTION

Wood/polyvinyl chloride (WPVC) composite is a type of wood/plastic composites (WPC) that is suitable for building and construction applications. WPVC has high stiffness, strong chemical resistance, and good flame retardation due to chlorine atoms in the PVC molecules. However, WPVC composites may be thermally unstable due to very poor thermal stability of the PVC, which may also be affected by the presence of wood fiber. Previous works by Sombatsompop et al. (2008) and Augier et al. (2007) revealed that the natural fiber or wood could accelerate the thermal degradation in PVC molecules. This led to quickly progressive discoloration and deterioration of the properties of WPVC composites. Therefore, more effective thermal stabilizers may be necessary for the formulation of the WPVC composites.

The thermal degradation process in PVC has been widely known to initiate at labile structures in the PVC chains, which were formed during polymerization. The main labile structures include allylic and tertiary chlorine atoms. The functions of thermal stabilizers for PVC involve displacing the labile chlorine atoms in PVC chains and trapping hydrochloric acid (HCl) gases that act as auto-catalyst. There are a number of published papers studying the stabilization efficiency of thermal stabilizers either acting alone and/or in mixtures on the improvement of thermal stabilities of PVC. The alkyltin alkyl thioglycolate stabilizers were found to be compatible with PVC over a broad concentration range, which led to higher thermal stabilization efficiencies (Safronov et al. 2003). The compatibility of alkyltin alkyl thioglycolate stabilizers with PVC decreased with increase of the alkyl chain length due to steric hindrance of alkyl radicals, reducing their interactions. The addition of mixtures of lead stearate and synthetic hydrotalcite into PVC improved the thermal and color stabilities of PVC as compared with the addition of either lead stearate or synthetic hydrotalcite alone (Kalouskova et al. 2004). Calcium and zinc stearates ($CaSt_2/ZnSt_2$) are recommended to be used in incorporating with other thermal stabilizers. Although the $CaSt_2/ZnSt_2$ stearates are non-toxic, they have poor long-term thermal stabilities (Wang et al. 2006; Fang et al. 2010). The effectiveness of $CaSt_2/ZnSt_2$ was synergized with the addition of pentaerythriol (PeE), whereas the addition of organotin was not found to have this effect (Wang et al. 2006). The stabilization efficiency of calcium stearate/zinc glutarate ($CaSt_2$/ZG) stabilizers to PVC could be obviously enhanced by the influence of lanthanum stearate ($LaSt_3$) as a co-stabilizer (Fang et al. 2010). The addition of di(ethyl hexyl) phthalate (DEHP) or epoxidized soybean oil (ESO) into the thermal stabilizer mixture of $CaSt_2/ZnSt_2$ could improve thermal stability of PVC and the intermediate $CaSt_2/ZnSt_2$ ratios could enhance the color stability of PVC (González-Ortiz et al. 2005).

There are a number of reports on the effects of wood fiber types, contents, shape characteristics, surface treatments, and processing conditions on the mechanical properties of wood plastic composites (WPC) (Bengtsson et al. 2006; Dobreva et al. 2006; Elgozali et al. 2007; Karmarkar et al. 2007; Tungjitpornkull et al. 2007; Faruk and Matuana 2008; Kalia et al. 2008; Rizvi and Semeralul 2008; Rahman et al. 2010), while little attention has been put on the thermal stabilities of WPC. Most research works on thermal stabilities of WPC were found in the case of using polyethylene (PE) or polypropylene (PP) as matrix (Kim 2003; Doh et al. 2005; Sailaja 2006; Doan et al. 2007; Nachtigall et al. 2007; Lei et al. 2007). The thermal stability of the natural fiber/PP or PE composites has been found to decrease as the natural fiber content is increased (Kim 2003; Doh et al. 2004). Coupling agents such as maleic anhydride grafted polypropylene (MAHgPP) and organosilane could slightly improve thermal stability of natural fiber/PP composites due to the stronger interaction between the fiber and matrix (Doan et al. 2007; Nachtigall et al. 2007). For WPVC composites, the research works on thermal stabilities of WPVC composites showed that the decomposition temperatures of WPVC composites were even lower than that of neat PVC (Sombatsompop et al. 2003, 2005, 2008; Ge et al. 2004; Augier et al. 2007). It was clearly suggested that the chlorine atoms in PVC could be cleaved easily due to presence of wood particles, resulting in production of polyene units in the PVC molecules (Sombatsompop et al. 2003, 2005). In addition, they also suggested that the additions of $ZnSt_2$ and lead stearate ($PbSt_2$) into WPVC composite could improve the thermal stability of the PVC in WPVC by retarding the upzipping reactions and by reducing the conjugated double bonds in PVC molecules.

This work is extended from previous work (Sombatsompop et al. 2008) in which it was found that $PbSt_2$ was the most effective thermal stabilizer but its disadvantage was toxicity of the Pb metal. Thus, the aim of the present work was to study the thermal stabilization of PVC in the WPVC composites by incorporating appropriate thermal stabilizers into the composites with idea of replacing the Pb stabilizer. The thermal stabilizers used, as compared with $PbSt_2$, in this work were calcium/zinc complex (Ca/Zn) stabilizer and methyl tin mercaptide (MT). Ca/Zn stabilizer was used because it is nontoxic and has a synergistic effect between $CaSt_2$ and $ZnSt_2$ (Vrandečić et al. 2001; Fang et al. 2010). On the other hand, MT was used due to its high stabilization efficiency, good compatibility with PVC (Safronov et al. 2003; Fang et al. 2010) and availability for food packaging in PVC (Gächter et al. 1990). The effects of thermal stabilizer type and content were assessed through structural changes in terms of polyene and carbonyl sequences, changes in decomposition temperature and physical appearances, and color changes by yellowness index (*YI*), as well as from visual photographs obtained for different thermal ageing times.

EXPERIMENTAL

Raw Materials

PVC

Suspension PVC was supplied by V.P. Wood Co., Ltd. (Bangkok, Thailand) in the form of powder, with the trade name SIAMVIC 258RB, and having a K value of 58. The PVC powder was dry-blended with various necessary additives as listed in Table 1, this being referred to as PVC compound.

Wood flour particles

Wood flour particles used in this work were supplied by V.P. Wood Co., Ltd. (Bangkok, Thailand); it had an average particle size of 100 to 300 μm. In this work, the content of wood flour particles in the PVC compounds was varied from 0, 50, and 70 parts per hundred resin (phr) of PVC powder, and the wood particles were chemically treated with 1.0 wt% *N-2*(aminoethyl)3-aminopropyl trimethoxysilane having a weight average molecular weight of 222.4. The detailed experimental procedure for the silane treatment was already given in our previous work (Sombatsompop and Chaochanchaikul 2005).

Thermal stabilizers

Three thermal stabilizers were used in this work; these being lead stearate ($PbSt_2$), calcium/zinc complex stabilizer or Ca/Zn (trade name as UNISTAB RCZ313P) and methyl tin mercaptide or MT. The $PbSt_2$ and Ca/Zn stabilizers in the form of powder were supplied by Evergreen Chemical Co., Ltd. (Thailand) and Sereechem Co., Ltd.

(Thailand), respectively. MT stabilizer was supplied in form of liquid by Thai Plastex Additives Co., Ltd. (Thailand). The content of thermal stabilizer used was varied as 0.0, 2.4, and 4.8 phr. In this work, influences of their chemical structure and mechanism on thermal stabilization of PVC into the neat PVC and WPVC composites were investigated by chemical degradation, physical appearances, and decomposition behavior.

Table 1. Materials Formulations for PVC Compound and WPVC Composites

Ingredients	Concentration (phr)
Suspension PVC (SIAMVIC® 258RB)	100.0
External lubricant (Finalux® G-741)	0.6
Calcium carbonate (Omyacarb® 2T)	12.0
Internal lubricant (Ca-St_2)	0.6
Processing aids (PA-20)	6.0
Natural filler (wood flour)	Varied (0, 50, 70)
Thermal Stabilizers (type and dosage) ➢ Lead stearate ($PbSt_2$) ➢ Ca/Zn complex (Ca/Zn) ➢ Methyl tin mercaptide(MT)	Varied (0.0, 2.4, 4.8)

Preparation of Test Specimen

Before blending wood flour and PVC compound, the wood flour was passed to heat treatment in an oven at 80 °C for 24 h until the weight of the wood was constant. After that the PVC compound was dry-blended with wood flour by a high speed mixer for 2 min before they were melt-blended in a twin screw extruder (Haake Polylab-Rheomex CTW 100P, Germany). The wood flour content added into the PVC compound was varied from 0 to 70 phr of PVC. The processing temperature profiles on the extruder were 160, 170, 170, and 180 °C from hopper to die zones. The screw speed was 30 rpm, and a slit die having width x height x length of 18.2 x 2 x 16 mm^3 was used to produce extrudates. The produced extrudates were then passed through a cooling system and sizing-control device before collection for thermal stability testing.

Characterization

Chemical degradation Analysis

Polyene and carbonyl indices were determined using attenuated total reflectance Fourier-transform infrared (ATR-FTIR) analysis to assess extent of degradation of the PVC and WPVC. This was carried out by measuring the reflectance difference percenttage at the surface of the specimen, which was prepared by a twin screw extruder as mentioned earlier. The dimensions of the specimen used (width x length x thickness) were 18 x 40 x 2 mm^3. These spectra were estimated using ATR-FTIR Spectrometer (Nicolet 6700 FT-IR spectrometer, USA). The polyene and carbonyl indices in this work were calculated by subtracting the value of % absorbance of the peak of interest ($\%A$ at wavenumber of 1630 and 1730 cm^{-1}, respectively) from the baseline ($\%A_{baseline}$) and dividing it by the reference value (%A_{2920}), which was also subtracted from the baseline (%$A_{baseline}$). The wavenumbers of 1630, 1730, and 2920 cm^{-1} were assigned for polyene sequences, carbonyl group, and C-H stretching, respectively. The detailed calculations can be found in our previous work (Sombatsompop et al. 2008).

Thermogravimeteric analysis

The decomposition temperature was analyzed with a TGA Instrument (Mettler Toledo TGA/SDTA 851^c, Columbus, OH). For comparison purposes, the decomposition temperature (T_d) results were taken when the maximum weight loss occurring during TGA runs. The derivative thermogravimetric (DTG) curves, the mass loss rate of specimen versus temperature, were reported. For operating steps, the first step was holding the temperature at 100 ^{o}C about 1 min to remove moisture and then the temperature was increased in the range of 100 to 600^{o}C with a heating rate of 10^{o}C/min.

Physical changes during thermal ageing

After processing, the neat PVC and WPVC specimens were aged in an oven operated according to ASTM D2115 (1992), by heating at 177 ^{o}C for various thermal ageing times (0, 30, 60, 120, 180, and 360 min). The color changes of the neat PVC and WPVC specimens were determined using two different color systems, the Munsell and CIE-LAB color system. In the Munsell color system, the *YI* and Hue were estimated by using a UV-Vis Spectrophotometer (Shimatsu UV-Vis 3100 Spectrophotometer, Japan) under the standard source C. The *YI* of aged specimens at different thermal ageing times was calculated according to the previous work (Sombatsompop et al. 2008). The lightness (L^*) of un-aged and aged PVC and WPVC specimens was estimated by using CIE-LAB color system under the D65 light source.

RESULTS AND DISCUSSION

Chemical Degradation Analysis

The chemical degradation of PVC in both neat PVC and WPVC composites was investigated by considering polyene and carbonyl indices with ATR-FTIR spectrometry. Figure 1 shows the effect of type and content of thermal stabilizers on the polyene index for neat PVC and WPVC composites. It was found that the addition of thermal stabilizer could enhance thermal stabilization of PVC in both neat PVC and WPVC composites by reducing the polyene content. The stabilizing mechanism involved displacing the labile chlorine atom in PVC chains and trapping HCl gases to retard the damaging autocatalytic action of HCl released by PVC chains (Kalouskova et al. 2004; Sombatsompop et al. 2008). The polyene content tended to decrease with changing dosages of thermal stabilizer from 2.4 to 4.8 phr. Among the three thermal stabilizers used, $PbSt_2$ was less effective than MT, but more effective than Ca/Zn, which was indicated by the polyene content for a given thermal stabilizer content. The stabilization mechanism by metal stearate ($PbSt_2$ and Ca/Zn) was that the metal stearate reacted with the PVC chains to retard the unzipping reaction by substituting the labile chlorine atoms with more stable stearate groups from the metal stearate, and also reacted with hydrogen chloride gas

(HCl) that were released from the dehydrochlorination process to form metal chloride (Sombatsompop et al. 2008). For Ca/Zn stabilizer, zinc chloride ($ZnCl_2$) produced from $ZnSt_2$ into Ca/Zn stabilizer by the above mentioned reaction could cause further rapid dehydrochlorination by acting as catalyst for degradation in PVC. This problem could be solved by the synergistic effect of combination with $CaSt_2$ (Vrandečić et al. 2001). $ZnCl_2$ could react with $CaSt_2$ by ester exchange reactions with $ZnCl_2$. In the case of $PbSt_2$ stabilizer, the lead chloride ($PbCl_2$) had slower effect on the PVC degradation than the $ZnCl_2$ in Ca/Zn stabilizer (Gächter et al. 1990; Sombatsompop et al. 2008). The PVC stabilization mechanism by MT also involved the displacement of labile chlorine atoms and reaction with HCl molecules (Safronov et al. 2003), this being similar to that by metal stearates mentioned earlier. The polyene result suggested that MT stabilizer exhibited the highest stabilization efficiency, as it has higher nucleophilicity of the mercaptide when compared with that of the carboxylate in the structure of metal stearate. Another reason involved an inherent compatibility of MT stabilizer with PVC resin due to an interaction between chlorine atoms of the PVC chain and tin in MT stabilizer (Safronov et al. 2003; Zweifel et al. 2009; Fang et al. 2010).

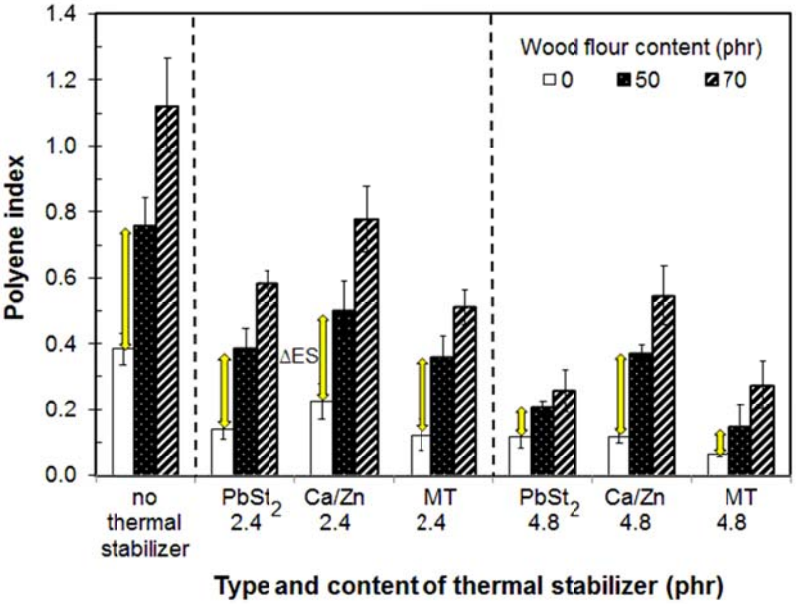

Figure 1. Polyene index of neat PVC and WPVC composites containing $PbSt_2$, Ca/Zn, and MT at dosage of 2.4 and 4.8 phr

For the effect of wood flour, it is shown in Fig. 1 that the polyene contents increased with increasing wood flour. This was propabably caused by moisture residue and hydroxyl (OH) groups on the wood surfaces. The moisture residue could be expected in wood flour by picking up moisture during storage and processing (Sombatsompop and Chaochanchaikul 2004). The OH groups in both moisture and the wood surface could interact with chlorine (Cl) atoms in PVC chains through polar-polar interaction so that Cl atoms could be more easily liberated from the PVC molecules and the HCl gas was then produced. The initial polyene sequences and HCl produced during processing could accelerate the rate of the dehydrochlorination reaction of PVC in WPVC composites, thus producing additional polyene sequences within the composite (Hjertberg et al. 1984; Sombatsompop and Chaochanchaikul 2004). The differences in polyene content (ΔES) between unfilled and wood-filled PVC became smaller with increasing the stabilizer dosages from 2.4 to 4.8 phr. This was probably because the stabilizers added into the composites were sufficient to reduce the HCl production and to retard the HCl acceleration, as discussed, even by the presence of wood.

Figure 2 shows carbonyl index for neat PVC and WPVC composites using the three thermal stabilizers at dosages of 2.4 and 4.8 phr. The influences of type and content of thermal stabilizer on the carbonyl content were similar to those on the polyene content. The higher the thermal stabilizer content the lower the carbonyl content. The efficiencies of thermal stabilizers on carbonyl content similar to polyene content were increased in order of MT > $PbSt_2$ > Ca/Zn stabilizers. However, it should be noted that if the formulations of PVC and wood/PVC composites are changed by adding more additives, the effectiveness order of these three stabilizers would be the same, but different values of polyene and carbonyl indices may be obtained.

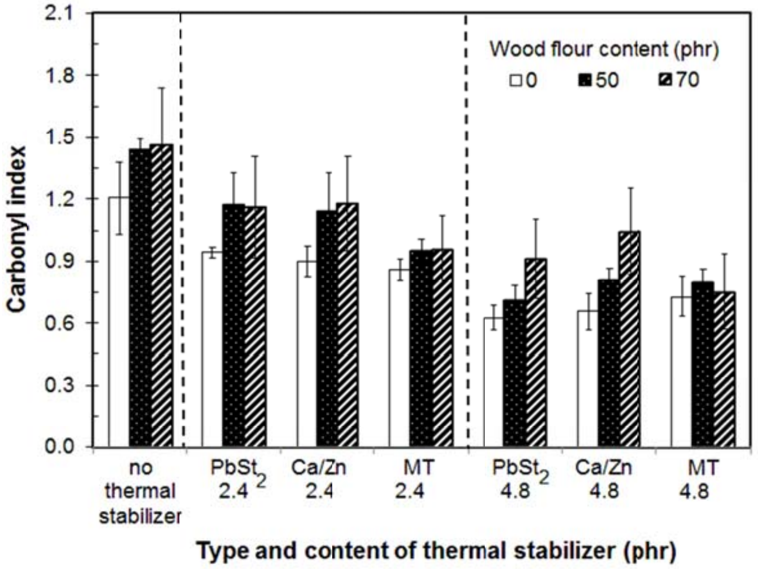

Figure 2. Effect of type and content of thermal stabilizers on carbonyl groups in neat PVC and WPVC composites

TGA Analysis

In addition to chemical degradation, the decomposition temperature and DTG curves from TGA technique could be used for estimating the stabilization efficiency of the thermal stabilizers. According to Fig. 1, the polyene contents for WPVC composites without thermal stabilizers were substantially high, and this resulted in severe thermal degradations (very poor process-abilities). Therefore, only decomposition temperature and DTG curve for neat PVC without thermal stabilizers were performed for comparison purposes. The results of T_d values at maximum %wt loss for neat PVC and WPVC composites with and without thermal stabilizers are given in Table 2.

Table 2. Effect of Type and Content of Thermal Stabilizer on the Decomposition Temperature for Neat PVC and PVC Containing Wood Flour 50 and 70 phr

Type and content of thermal stabilizer	Decomposition Temperature at maximum %wt. loss (^oC)		
	neat PVC	PVC with wood flour at 50 phr	PVC with wood flour at 70 phr
no thermal stabilizer	294.5	NA	NA
PbSt2 2.4 phr	296.0	273.5	269.0
Ca/Zn 2.4 phr	295.5	265.5	266.0
MT 2.4 phr	317.0	275.5	270.5
PbSt2 4.8 phr	308.5	274.5	269.5
Ca/Zn 4.8 phr	295.5	265.0	263.0
MT 4.8 phr	315.5	278.0	271.5

NA = could not be processed.

For neat PVC, the T_d values of PVC stabilized with thermal stabilizers were higher than that of non-stabilized PVC. The order of T_d values in PVC stabilized with three different thermal stabilizers corresponded to that of polyene and carbonyl indices by increasing in the order of MT > $PbSt_2$ > Ca/Zn. The PVC stabilized with MT had the highest T_d value, indicating that MT performed as the most effective stabilizer. This might be attributed to higher nucleophilicity of the mercaptide in the MT structure as compared to that of carboxylate in the structure of metal stearate. The differences in nucleophilicities of these two stabilizer types (MT and metal stearate) involved differences in polarizabilities of the electron densities as a result of sulfur atoms in MT and oxygen atoms in metal stearate (Zweifel et al. 2009). For the effect of wood flour, it could be seen that the T_d values of WPVC composites for both wood contents of 50 and 70 phr were lower than those of neat PVC. This was because the partial wood flour was decomposed and the presence of wood flour could accelerate the PVC degradation. The thermal decomposition of most natural fiber occurred within a temperature range between 215 and 310^oC (Yao et al. 2008). From the polyene content, it was found that the presence of the wood induced the thermal degradation of PVC in the WPVC composites to occur faster, and the initial polyene sequences and HCl produced during processing could accelerate the rate of the dehydrochlorination reaction of PVC in WPVC composites (Sombatsompop and Chaochanchaikul 2004). For the effect of thermal stabilizer, the order of T_d values in WPVC composites was the same as observed in neat PVC, but the differences in T_d values between three different thermal stabilizers decreased with increasing wood content. This was because the presence of wood flour has suppressed the substitution ability of the thermal stabilizer in the PVC chains.

Figure 3 shows DTG curves used for evaluating the efficiency of the thermal stabilizers. For neat PVC shown in Figs. 3a and 3d, MT stabilizer was observed to be the most effective stabilizer, considered by the rate of mass loss and the shift of the DTG curves. The efficiencies of the three thermal stabilizers estimated by DTG curve were in the same order as the decomposition temperature and polyene and carbonyl indices. For the stabilization efficiencies of thermal stabilizers in WPVC composites at wood contents of 50 and 70 phr shown in Figs. 3b and 3e and Figs. 3c and 3f, respectively, it was found that MT stabilizer was still the most effective thermal stabilizer, as it was in neat PVC. For WPVC composites, the differences in the effectiveness of these three thermal stabilizers could not be seen obviously as compared to those in the case of neat PVC due to the presence of wood flour, which accelerated the thermal degradation of PVC and also suppressed the stabilization abilities of the thermal stabilizers as mentioned above.

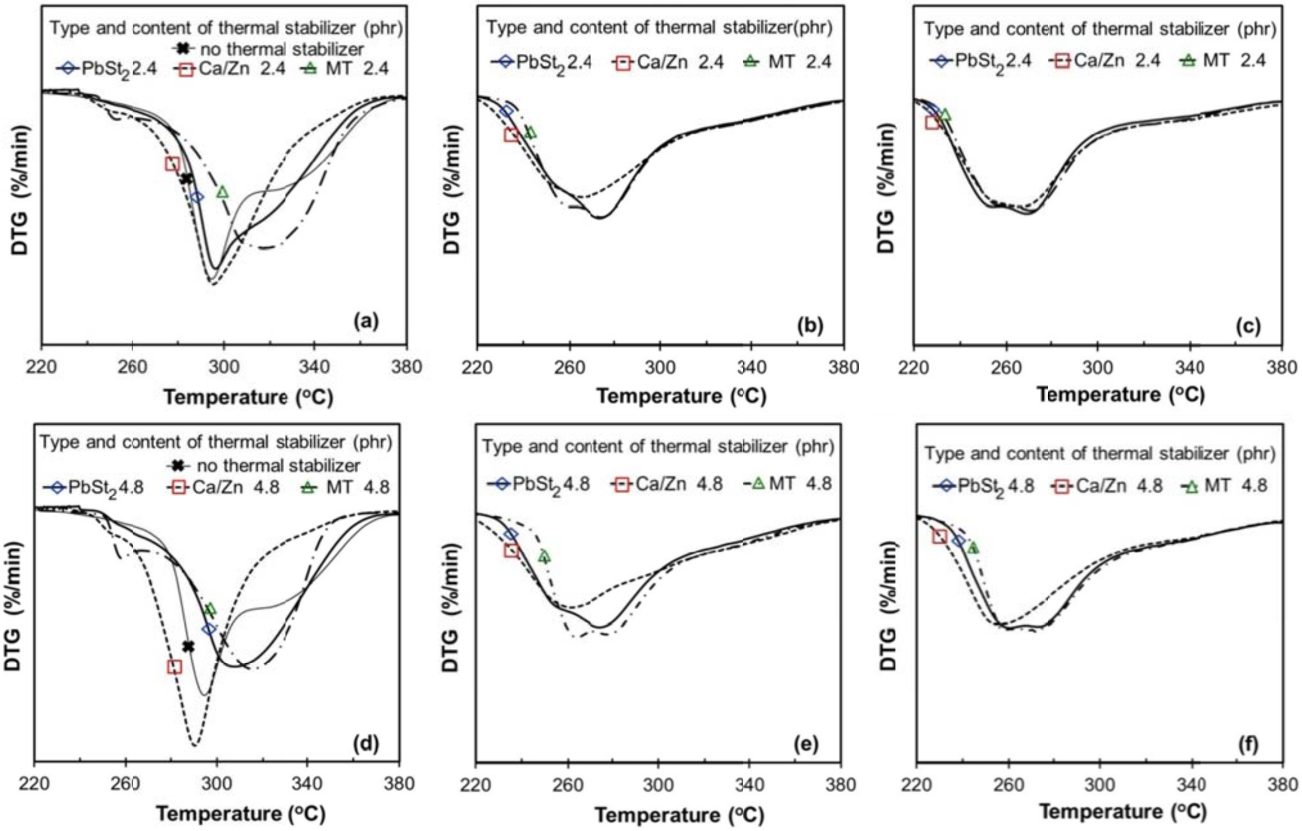

Figure 3. DTG curves of neat PVC and WPVC composites with three thermal stabilizers: wood flour at 0 phr (a and d), 50 (b and e), and 70 phr (c and f)

Physical Appearances under Thermal ageing

Physical appearances of neat PVC and WPVC composites with different thermal stabilizers at various thermal ageing times were assessed by measuring yellowness index (*YI)*, Lightness (*L**), Munsell Color System (color shade) and visual photographs. Figure 4 shows the *YI* results for neat PVC and WPVC composites for different ageing times at 177°C. Figure 4a reveals that the lower *YI* of neat PVC with addition of thermal stabilizers resulted from turning white color of the stabilized PVC. For thermal aged conditions, the *YI* for non-stabilized PVC decreased with increasing ageing time, whereas the *YI* for PVC stabilized with $PbSt_2$ or Ca/Zn increased at the initial ageing times and then decreased at high ageing times (180 to 360 min). The increase of *YI* for PVC stabilized with $PbSt_2$ or Ca/Zn indicated the color changing from white to yellow, whereas the decrease of *YI* indicated the color change to brown or dark. In the case of MT stabilized PVC, the color of MT stabilized PVC specimen after ageing was similar to that of the un-aged specimen. For the effect of thermal stabilizer, the higher the thermal stabilizer, the lower the magnitude of change in *YI*. By considering the *YI* values, it could be stated that MT stabilizer was the most effective thermal stabilizer in this work for stabilizing the PVC under the test temperature of 177^{o}C. For WPVC composites in Figs. 4b and 4c, it was found that the initial *YI* values for all cases were slightly different and were higher than those for the neat PVC due to that the initial color of wood particles themselves. Under the aged condition, the *YI* of WPVC composites decreased as ageing time was increased. The decreases in *YI* might be caused by the acceleration effect by wood flour on the PVC degradation and the degradation of wood particles themselves. The most effective thermal stabilizer for WPVC was still MT stabilizer. It was also noted that the effect of thermal stabilizer content on the *YI* for WPVC composites were not very pronounced, and this may be associated with the suppressing effect by the wood presence in the composites.

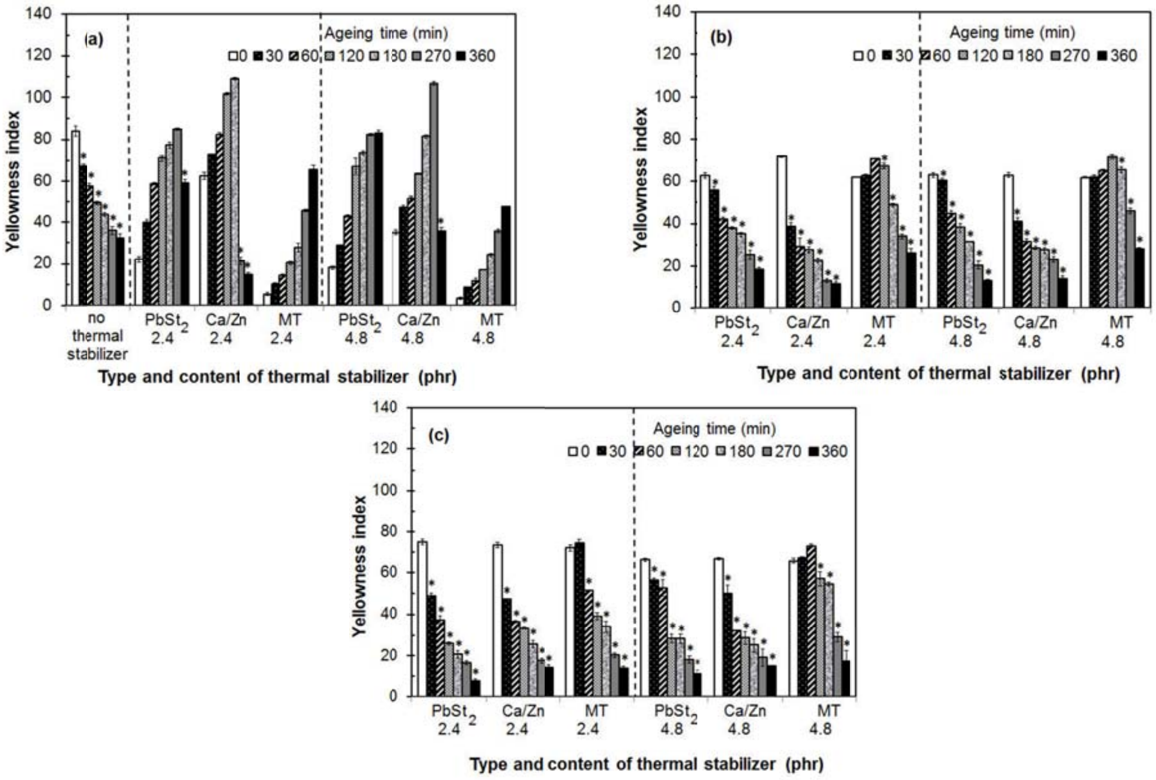

Figure 4. Yellowness index of neat PVC and WPVC composites with three thermal stabilizers at different ageing times at 177^{o}C : wood flour at (a) 0 phr, (b) 50 phr, and (c) 70 phr (* specimens turning dark color)

Table 3 shows the hue values in the Munsell Color System for neat PVC and WPVC composites at different ageing times. The Hue values in this work were found in the color shade ranges of green yellow (GY), yellow (Y), yellow red (YR), and red (R). It was found in Table 3a that the initial color (before ageing) of non-stabilized PVC was YR, whereas the initial colors of PVC stabilized with MT or PbSt$_2$ were in the color shade of GY and that of Ca/Zn stabilized PVC was Y. The color shades of YR and R for aged PVC were found in case of PVC stabilized with $PbSt_2$ and Ca/Za at high ageing times of 270 to 360 min. The MT exhibited the most resistance to thermal degradation of the PVC by considering the color shade without changing to became YR. Table 3a suggests that the colors for neat PVC due to thermal ageing changed from GY→Y, Y→YR, and YR→R, whereas those for WPVC composites exhibited YR only. However, the hue value for the YR color for WPVC composites progressively decreased (from ~8 to 2), indicating that the specimen color became more reddish. This phenomenon is seen in Tables 3b and 3c. It was also found that the initial color shades of WPVC composites were slightly different by changing the type and content of thermal stabilizers. The visual photographs of neat PVC and WPVC composites as shown in Fig. 5 corresponded to the hue values as given in Table 3.

Table 3a. Hue Values for Neat PVC Containing $PbSt_2$, Ca/Zn and MT at Dosage of 2.4 and 4.8 phr

Ageing time (min)	Hue values						
	no thermal stabilizer	$PbSt_2$ 2.4 phr	Ca/Zn 2.4 phr	MT 2.4 phr	$PbSt_2$ 4.8 phr	Ca/Zn 4.8 phr	MT 4.8 phr
0	1.8YR	0.6GY	4.7Y	6.0GY	9.1Y	7.8Y	7.7GY
30	2.0YR	6.8Y	2.8Y	2.2GY	7.4Y	5.6Y	3.2GY
60	1.4YR	3.5Y	0.4Y	1.7GY	5.1Y	4.6Y	2.6GY
120	1.0YR	0.7Y	6.3YR	0.8GY	0.8Y	3.6Y	1.6GY
180	1.4YR	8.6YR	3.4YR	9.8Y	8.0YR	1.2Y	0.0GY
270	1.6YR	5.4YR	0.8YR	5.9Y	5.3YR	7.1YR	7.5Y
360	1.6YR	8.6R	10.0R	3.4Y	6.0YR	0.1YR	4.9Y

Table 3b. Hue Values for WPVC Composites at Wood Content of 50 phr Containing $PbSt_2$, Ca/Zn and MT at Dosage of 2.4 and 4.8 phr

Ageing time (min)	Hue values					
	$PbSt_2$ 2.4 phr	Ca/Zn 2.4 phr	MT 2.4 phr	$PbSt_2$ 4.8 phr	Ca/Zn 4.8 phr	MT 4.8 phr
0	8.4YR	8.1YR	8.6YR	8.5YR	8.4YR	8.3YR
30	3.6YR	1.6YR	8.5YR	4.2YR	2.9YR	8.3YR
60	3.0YR	1.8YR	7.6YR	3.0YR	2.7YR	8.3YR
120	2.2YR	2.1YR	3.5YR	3.0YR	3.0YR	6.1YR
180	2.5YR	2.7YR	2.5YR	2.9YR	3.7YR	3.2YR
270	2.8YR	2.7YR	2.5YR	2.9YR	3.5YR	1.8YR
360	2.2YR	2.8YR	2.2YR	2.1YR	3.1YR	1.3YR

Table 3c. Hue Values for WPVC Composites at Wood Content of 70 phr Containing $PbSt_2$, Ca/Zn and MT at Dosage of 2.4 and 4.8 phr

Ageing time (min)	Hue values					
	$PbSt_2$ 2.4 phr	Ca/Zn 2.4 phr	MT 2.4 phr	$PbSt_2$ 4.8 phr	Ca/Zn 4.8 phr	MT 4.8 phr
0	7.9YR	7.7YR	8.2YR	8.2YR	8.0YR	8.2YR
30	2.3YR	2.6YR	7.7YR	4.6YR	2.7YR	8.2YR
60	2.5YR	2.2YR	2.7YR	3.5YR	2.7YR	7.3YR
120	3.0YR	2.2YR	2.9YR	3.1YR	2.9YR	3.3YR
180	3.1YR	2.5YR	2.6YR	2.8YR	3.5YR	3.0YR
270	2.4YR	3.4YR	2.3YR	2.6YR	3.4YR	2.3YR
360	2.1YR	2.9YR	2.1YR	2.4YR	2.9YR	2.5YR

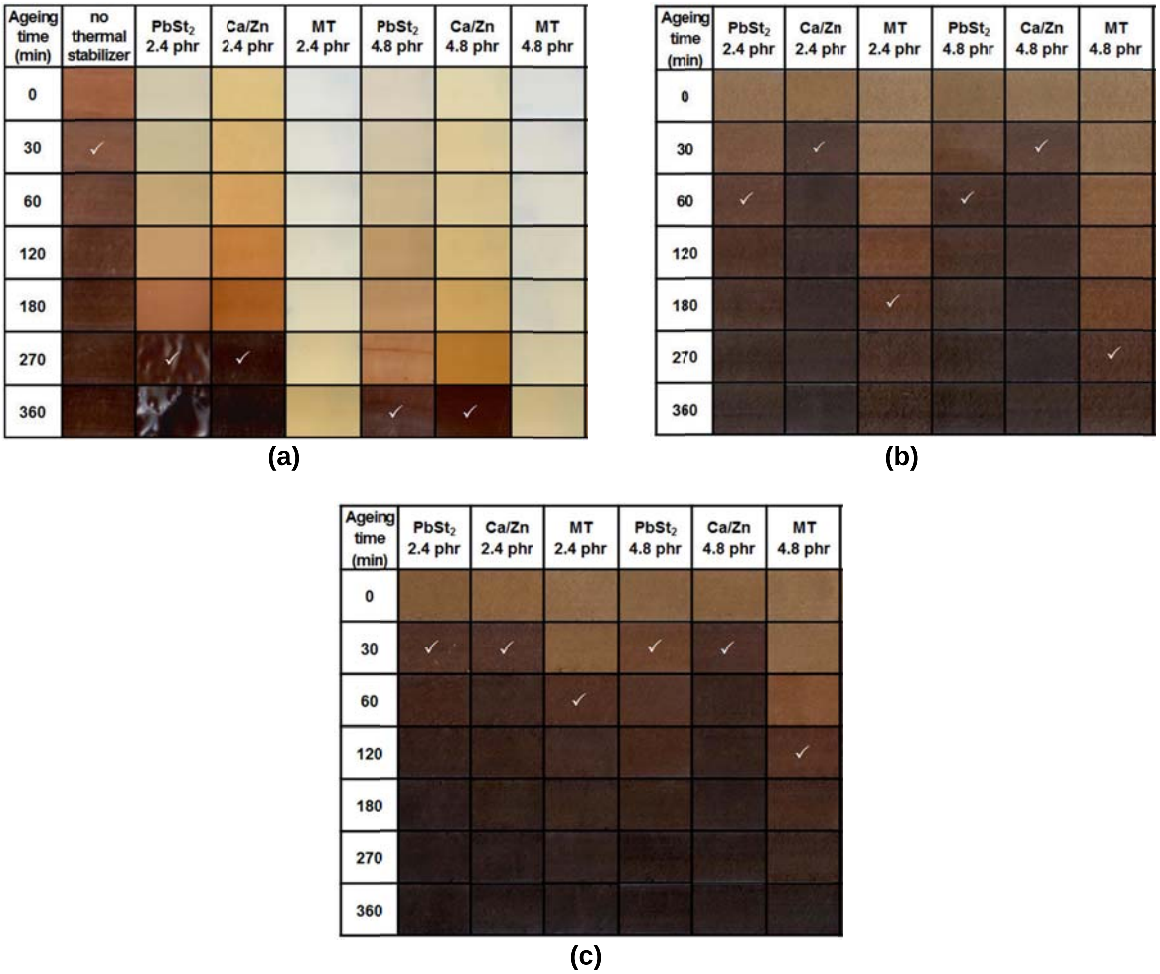

Figure 5. Digital photographs for neat PVC and WPVC composites containing $PbSt_2$, Ca/Zn and MT at dosage of 2.4 and 4.8 phr: wood flour at (a) 0 phr, (b) 50 phr and (c) 70 phr

Figure 5 also shows that the colors of PVC stabilized with $PbSt_2$ and Ca/Za became brown or dark at high ageing times, whereas that of the PVC stabilized with MT did not change. For WPVC composites, the color of WPVC stabilized with $PbSt_2$ and Ca/Za became dark at the initial ageing times (30 to 60 min), whereas that of WPVC stabilized with MT became dark at higher ageing times, suggesting more effective stabilizing of the MT stabilizer. The color changes toward brown or dark are marked as (✓). Increasing thermal stabilizer content led to the slower color change (i.e., longer time to color change). The visual photographs of un-aged and aged WPVC composites indicated that the content and type of thermal stabilizer affected only the color of the aged WPVC specimens. MT was again the most suitable thermal stabilizer for stabilizing the PVC in WPVC composites under the thermal ageing.

Figure 6 shows the lightness (L^*) as a function of thermal ageing time for neat PVC and WPVC composites with three different thermal stabilizers.

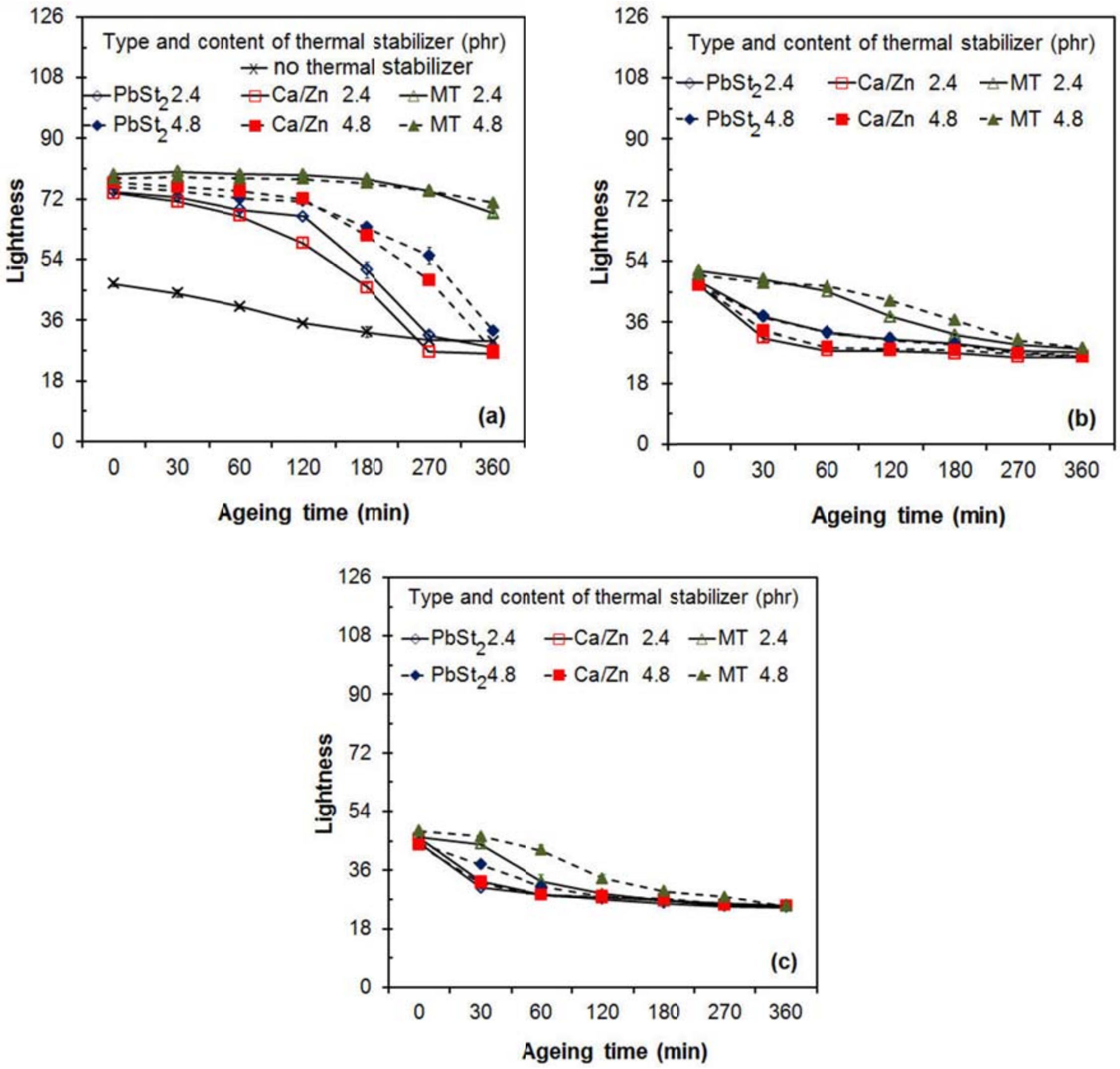

Figure 6. Lightness for neat PVC and WPVC composites containing $PbSt_2$, Ca/Zn and MT at dosage of 2.4 and 4.8 phr: wood flour at (a) 0 phr, (b) 50 phr, and (c) 70 phr

It was noticeable that the L^* for both neat PVC and WPVC composites decreased with increasing ageing time due to the color change of PVC from white to yellow or brown as mentioned earlier. For the effect of thermal stabilizers, it was observed that the type and content of thermal stabilizers slightly affected the initial L^* values for both neat PVC and WPVC composites. The initial L^* value of non-stabilized PVC was lower than that of stabilized PVC. The effects of type and content of thermal stabilizers on L^* at different ageing times were similar to that on the *YI*. The changes in L^* for both neat PVC and WPVC specimens with three different thermal stabilizers increased in the order of Ca/Zn > $PbSt_2$ > MT.

CONCLUSIONS

In this work, thermal and structural stabilities of PVC in neat PVC and WPVC composites were assessed through the use of three different thermal stabilizers. The experimental results suggested that the three thermal stabilizers could improve the thermal stabilities of PVC in neat PVC and WPVC composites *after processing*. In this work, MT was found to be the most suitable stabilizer, considering the polyene and carbonyl contents, the decomposition temperature, and the shift of DTG curves. MT stabilizer could also be used to replace the toxic $PbSt_2$. The addition of wood particles resulted in increases in polyene and carbonyl sequences during processing and decreased T_d values. The stabilization efficiencies of the MT, $PbSt_2$, and Ca/Zn stabilizers were reduced and suppressed by the presence of wood particles in PVC compounds. Increasing thermal stabilizer could moderate the thermal degradations of PVC and WPVC composites.

For thermal and structural stabilities of PVC *after prolonged thermal ageing at 177°C* evaluated through the Munsell and the CIE-LAB color systems, the *YI* for stabilized PVC with thermal stabilizers increased and then decreased at high ageing times (180 to 360 min). The *YI* values of WPVC composites decreased with increasing ageing time. The decrease of *YI* indicated the production of polyene groups in PVC leading to the color change from yellow to brown or dark. MT was still the most suitable stabilizer for WPVC composites under the prolonged aged conditions.

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