Improvement of Structural and Thermal Stabilities of PVC and Wood/PVC Composite by Zn and Pb Stearates, and Zeolite

Narongrit Sombatsompop[a]; Kulnida Taptim[a]; Kantima chaochanchaikul[a]; Chanchai Thongpin[b]; Vichai Rosarpitak[c]

[a] Polymer Processing and Flow (P-PROF) Group, School of Energy, Environment and Materials, King Mongkut's University of Technology, Bangmod, Bangkok, Thailand [b] Faculty of Engineering and Industrial Technology, Department of Materials Science and Engineering, Silpakorn University, Nakornpathom, Thailand [c] V.P. Wood Co., Ltd., Thungkru, Bangkok, Thailand

PLEASE SCROLL DOWN FOR ARTICLE

Improvement of Structural and Thermal Stabilities of PVC and Wood/PVC Composite by Zn and Pb Stearates, and Zeolite

NARONGRIT SOMBATSOMPOP,[1] KULNIDA TAPTIM,[1] KANTIMA CHAOCHANCHAIKUL,[1] CHANCHAI THONGPIN,[2] and VICHAI ROSARPITAK[3]

[1]*Polymer Processing and Flow (P-PROF) Group, School of Energy, Environment and Materials, King Mongkut's University of Technology, Bangmod, Bangkok, Thailand*
[2]*Faculty of Engineering and Industrial Technology, Department of Materials Science and Engineering, Silpakorn University, Nakornpathom, Thailand*
[3]*V.P. Wood Co., Ltd., Thungkru, Bangkok, Thailand*

Three different chemical stabilizers were introduced into neat PVC and a wood/PVC composite (containing 50 phr wood flour) to improve their thermal and structural stabilities. The changes in CIE yellowness index, polyene index, %wt loss, and decomposition temperature (T_d) were monitored. The effects of type and content of thermal stabilizers, thermal ageing time, and the presence of wood flour were our main interests. The experimental results suggested that the additions of Zn and Pb stearates into PVC and wood/PVC composite could improve the thermal stability of the PVC. At the test temperature of 177°C, the additions of Zn and Pb stearates could improve the thermal stabilities of PVC by retarding the upzipped reaction and by reducing the conjugated double bonds in PVC, Pb stearate being the most suitable for thermally stabilizing the PVC. Around the T_d range (~264°C), the addition of Zn stearate reduced the T_d value of PVC whereas that of Pb stearate had no effect on the change in T_d value. Zeolite loading could shift the T_d value of the PVC from 264 to 280°C. The addition of wood particles increased the polyene content and decreased the decomposition temperature of the PVC. The effect of wood flour on the thermal and structural changes of PVC overruled that of thermal stabilizer loading.

Keywords: poly(vinyl chloride); wood flour; thermal stabilizer; composite; extrusion

1 Introduction

Poly(vinyl chloride) (PVC) is one of the most widely used thermoplastics, but its thermal stability is very poor. Therefore, the addition of thermal stabilizers is necessary during processing. The degradation of PVC proceeds by a dehydrochlorination process resulting in the formation of long conjugated double bonds or polyene sequence (-CH=CH-)$_n$ and the release of gaseous hydrogen chloride (HCl). This leads to progressive resin discoloration, degradation of the polymer backbone, and ultimately deterioration of the polymer properties. Thermal stabilizers are most commonly used in PVC compounds. Their operation involves a reaction with HCl. The commercial thermal stabilizers used

for PVC include metal soaps (lead, calcium, zinc, barium, aluminum and their composites), organotin compounds, organic stabilizers and inorganic stabilizers (zeolite and hydrotalcite). Metal soaps are used to displace the labile chlorine atom in PVC polymer chains by the ester from the decomposed stabilizer to stabilize the PVC. In addition, they can trap HCl gases to retard the damaging autocatalytic action of HCl released by PVC chains (1–5). Zeolite, an acid absorber, can also stabilize the PVC due to absorption of the evolved HCl (2). There are a number of published papers studying the effects of thermal stabilizers on improvement of thermal stabilities of PVC. Kalouskova et al. (1). investigated the effect of lead stearate and synthetic hydrotalcite, alone and in mixed cases, on the stability of PVC during heat treatment. They found that the addition of mixtures of lead stearate and synthetic hydrotalcite increased the thermal and color stabilities of PVC as compared with the addition of either lead stearate or synthetic hydrotalcite alone. Atakul et al. (2) found that using suitable amounts of zeolite and zinc stearate as costabilizer in PVC plastigel could lead to a synergistic effect on thermal stability of PVC. The most recent work, by Liu et al. (5), investigated

Address correspondence to: Narongrit Sombatsompop, Polymer Processing and Flow (P-PROF) Group, School of Energy, Environment and Materials, King Mongkut's University of Technology, Thonburi (KMUTT) Thongkru, Bangmod, Bangkok 10140, Thailand. Tel.: (662) 470-8645; Fax: (662) 470-8647; E-mail: narongrit.som@kmutt.ac.th

the performance of hydroxylbenzylthioethers employed as organic thermal stabilizers for rigid poly(vinyl chloride) and their efficiencies were compared with Ca-Zn soap and methyltin stabilizers. They found that hydroxylbenzylthioethers exhibited greater efficiency than the other two, this being attributed to the ability of these compounds to prevent the formation of polyene sequences. The hydroxylbenzylthioethers-stabilized PVC showed a slightly lower glass transition temperature in comparison with the original PVC compound.

Wood-polymer composite (WPC) products have been increasingly used in various applications because of cost savings, good mechanical properties, better dimension stability, environmentally friendly products, and low density as compared with use of synthetic-fiber and thermoplastic composites. Applications of the WPC products include decking, window and door profiles, automobile paneling, panel inserts, and flower pots. Wood-PVC composite products have a number of advantages over composite products from wood with other thermoplastics in terms of higher mechanical strength and ignition resistance and better flame retardation due to chlorine atoms in the molecules. However, wood-PVC composite products may be thermally and photochemically unstable by undergoing an autocatalytic dehydrochlorination reaction under heating and UV-light conditions, which quickly deteriorates the composite properties (6, 7). There are a number of reports on the effects of wood fiber types, contents, shape characteristics, surface treatments and processing conditions on the properties (mechanical, thermal, physical and morphological) of natural fiber/PVC composites (8−14) while little attention has been put on the thermal stability of PVC in wood-PVC composites. Matuana et al. (6, 7) studied the ultraviolet weathering performance of wood/PVC composites and found that the addition of wood fiber had a deleterious effect on the ability of the PVC to resist degradation, but the UV stability of the composites could be improved by the incorporation of rutile-titanium dioxide pigment. Work by Sombatsompop et al. (9) has 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. This work is extended here by attempting to thermally stabilize the PVC in the wood-PVC composites by incorporating suitable thermal stabilizers into the composites.

As indicated above (1−5), there have been a number of published papers on the effects of incorporating different thermal stabilizers on the thermal stabilities of neat PVC, but those on the thermal stabilities of the PVC in wood-PVC composites are rare and still open for discussion among scientists and technologists. In this work, three different chemical stabilizers were introduced into both neat PVC compound and wood/PVC composite, and the thermal and structural stabilities of the PVC were monitored through the changes in CIE yellowness index, polyene sequences, percentage weight loss (rate of decomposition), and decomposition temperature. The effects of type and content of thermal

Table 1. The ingredients of PVC compounds and composites

Ingredients	Concentration (phr)
Suspension PVC grade SIAMVIC® 258RB	100.0
External lubricant (Finalux® G-741)	0.6
Calcium carbonate (Omyacarb®-2T)	12.0
Processing aids (PA-20)	6.0
Wood flour	0 and 50
Thermal stabilizers (Pb or Zinc stearate or Zeolites)	Varied (0, 2.4, 4.8)

stabilizers, thermal ageing time and the presence of wood flour were our main interest in this work. The stabilizing mechanisms of all thermal stabilizers used in the compound and composite were proposed and discussed.

2 Experimental

2.1 Raw Materials

The ingredients of the PVC compounds and composites are shown in Table 1. Suspension PVC was supplied by Vinyl Thai Co., Ltd. (Bangkok, Thailand) in the form of powder; the trade name was SIAMVIC-258RB with K value of 58. The PVC powder was dry-blended with various additives, as listed, to give PVC compounds. Wood particles were obtained from carpentry and wood-working processes and supplied by V.P. Wood Co., Ltd. (Bangkok, Thailand). The average size of the wood particles used in this work was in the range of 150−250 μm. Since previous works (7−9, 11) had extensively studied the effect of wood flour content on thermal and mechanical property changes of PVC in wood/PVC composites, the wood flour content added into the PVC compound in this work was fixed at 50 parts per hundred (phr) of PVC.

Three stabilizers were used in this study: namely; lead (Pb) stearate, and zinc (Zn) stearate, and zeolite; their chemical structures are listed in Table 2. Zeolite stabilizer was supplied by The PQ Chemical Co., Ltd. (Thailand) and both Pb and Zn stearates were supplied by Evergreen Chemical Co., Ltd. (Thailand). With these stabilizers, the influence of the chemical structure and their stabilization mechanisms on thermal stabilities of PVC in wood-PVC composites could be investigated.

Table 2. Chemical structures of thermal stabilizers used

Stabilizer	Chemical structure
Zn stearate	$Zn(C_{17}H_{35}COO)_2$
Pb stearate	$Pb(C_{17}H_{35}COO)_2$
Zeolite	$\{Na_{12}\,[Al_{12}Si_{12}O_{48}] \cdot 27H_2O\}_8$

2.2 Preparation of Composite Specimens

Before blending the wood particles and PVC compound, the wood particles were subjected 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 the 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 blending temperature profiles on the extruder were 165, 175, 175 and 185°C from hopper to die zones. The screw rotation speed was 40 rpm, and a slit die having width x height x length of $18.2 \times 2 \times 16$ mm^3 was used to produce slit extrudates. The extrudates were then passed through a cooling-system and sizing-control device before collection for thermal stability studies.

2.3 Characterizations

2.3.1 Thermogravimetric Analysis

The decomposition temperature (T_d) was analyzed with a TGA Instruments (Perkin-Elmer TGA7, Boston, MA). For comparison purposes, the onset of decomposition temperature (T_d) was taken when the 10% wt loss had occurred during the TGA runs. The temperature was first held at 100°C about 1 min for removing moisture. After that, the temperature was increased from 100 to 700°C with a heating rate of 5°C/min.

2.3.2 Chemical Degradation Analysis

Polyene sequences (ES) were determined using attenuated total reflectance Fourier-transform infrared (ATR-FTIR) analysis to assess the extent of degradation of the PVC in the mixture. This was carried out by measuring the reflectance difference percentage at the surface of the specimen, which was prepared by the twin screw extruder as mentioned earlier. The dimensions of the samples were prepared as 13 mm wide, 64 mm long and 2 mm thick. The tests were performed using FTIR Spectrometer (Nexus 470-FTIR Spectrometer, Wisconsin, USA) to produce spectra of reflectance against wave number. In this work, polyene sequences (ES) were calculated by subtracting the value of % reflectance of the peak of interest ($\%R_{1629}$) from the baseline ($\%R_{baseline}$) and dividing it by the reference value ($\%R_{2912}$) subtracted from the baseline ($\%R_{baseline}$) as shown in Equation (1) (15). The two different wave numbers followed were 2912 and 1629 cm^{-1} for C-H stretching and polyene sequences (ES), respectively.

$$\text{Polyene sequence (ES)} = \frac{\%R_{baseline} - \%R_{1629}}{\%R_{baseline} - \%R_{2912}} \qquad (1)$$

2.3.3 Discoloration Test

After processing, thermal stabilities were investigated according to ASTM D2115 (1992) by heating the neat PVC and wood-PVC composite samples at 177°C for various thermal ageing times (0, 30, 45, 60, 90, 120, 180, 270 and 360 min). The color changes of the PVC compounds were determined using two different color systems, the DataColor CIE LAB System (GretagMacbeth; Color-Eye 3100), and the Munsell Color System, color differences between the measured compound and the control compound under normally visible light were determined (using D_{65} as illuminant type) (16). The thermally aged specimens were evaluated using a UV-Vis Spectrophotometer (Shimatsu UV-Vis 3100 Spectrophotometer, Japan) according to the standard of the CIE LAB System for measuring X, Y and Z tristimulus values to calculate the CIE yellowness index as shown in Equation (2) (17). For the Munsell color system (18), only the Hue index was considered.

$$YI = \frac{100(1.28X_{CIE} - 1.06Z_{CIE})}{Y_{CIE}} \qquad (2)$$

2.3.4 SEM Investigations

The morphological structure of the wood/PVC composites was investigated using a JEOL (JSM-6301F) SEM machine at 15 kV accelerating voltage. The details of the experimental procedure and sample preparations are given elsewhere (9, 11).

3 Results and Discussion

Figure 1 shows the changes in CIE yellowness index of neat PVC compound for various aging times ranging from 0 to 270 min for three different thermal stabilizers at 2.4 and 4.8 phr loadings. Since only the yellow-to-dark zone of PVC color change was considered, decreasing CIE yellowness index on the x-axis simply indicates a degradation of PVC (changing of the sample color from yellow to dark).

Unaged condition: Considering the CIE yellowness index for un-aged samples (0 min), the additions of Zn and Pb stearates resulted in a color change in the PVC while the addition of zeolite had no effect. The lower CIE yellowness index for the PVC compound with added Zn and Pb stearates in this stage (un-aged) resulted from the color of the Zn and Pb stearates, the PVC compounds turning white after these additions.

Aged condition: During the experiment, it was observed that in the ageing time of less than 30 min, the differences in the CIE yellowness results of PVC among the three stabilizers used were not obvious. Therefore, the CIE results were reported only after the ageing time from 30 to 270 min. The degradation reaction of PVC in the initial ageing time (less than 30) may have been retarded by the presence of the stabilizers used. The results in Figure 1 show that during the thermal ageing from 30 to 270 min, the non- and zeolite-stabilized PVC samples showed a progressive decrease in the CIE index (starting at 30 min) which indicated a progressive degradation of the PVC. The degradation of PVC is usually explained by a dehydrochlorination process, involving the formation of long conjugated double bonds or
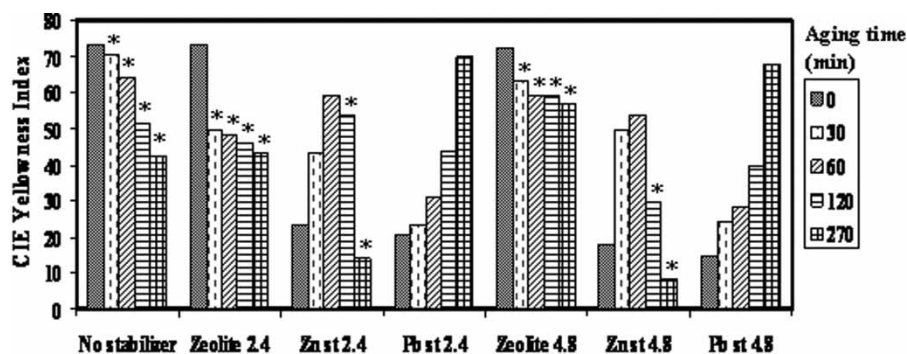
Fig. 1. CIE yellowness index of neat PVC with Zn, Pb and zeolite stabilizers for different ageing times at 177°C (* specimens turning brown color).

polyene groups (-CH=CH-)$_n$. The occurrence of the polyene groups in the PVC compound leads to the color change, usually turning into brown or dark. Figure 1 also shows that the color of the PVC samples with added Zn stearate changed from white to yellow in the first 60 min of ageing time and then, apparently, degraded (turning brown) at higher ageing times (120–270 mn). In the case of Pb stabilized PVC compound, no obvious degradation was observed for the whole period of ageing times studied although the samples turned yellow with increasing ageing time; the color of the Pb stabilized PVC sample after ageing was similar to the unaged sample with no brown color observed. Although the PVC samples with Pb or Zn stearates started out white, it could be confidently stated that both stearates could improve or prolong the resistance to thermal degradation as compared with zeolite and non-stabilized ones. Specifically, Pb stabilizer was regarded the most suitable of our additives for thermally stabilizing the PVC under the test temperature of 177°C. This statement appears to be true when considering the color change of PVC with Zn stearate after high ageing time of greater than 120 min.

It should be noted that the CIE index cannot be used alone to monitor the degradation of the PVC in the Zn and Pb stabilization systems, due to the fact that the starting CIE indexes (white color) of these compounds were different from those of the non- and zeolite stabilized PVC compounds. Therefore,
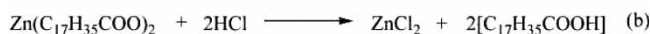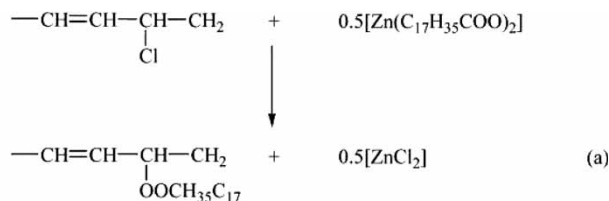
the Munsell Colors System was used for quantitative evaluation of the PVC degradation with the various thermal stabilizers; the results are shown in Table 3. The Zn and Pb stearates prolonged the resistance to thermal degradation of the PVC, the color of the PVC compounds remaining yellow (Y) for the whole period of ageing times used (greater than 30 min). In the case of non- and zeolite-stabilized PVC compounds, the color of the PVC changed from yellow-red (YR) to red (R) after thermal ageing. In addition, increasing the dosages of Pb stearate from 2.4 to 4.8 phr improved the thermal stability of the PVC. The Munsell results also re-confirmed that Pb stearate was the most suitable thermal stabilizer in this work.

The mechanisms of PVC stabilization by Zn and Pb stearates are illustrated by Schemes 1 and 2, respectively. Scheme 1 shows that Zn stearate can react with the PVC main-chains to retard the unzipping reaction by substituting the Cl atom with stearate group from the Zn stabilizer (Scheme 1a) and, with the HCl released from the dehydrochlorination process, to form $ZnCl_2$ molecules (Scheme 1b) (19). In the normal dehydrochlorination process, the released HCl could induce Cl cleavage from the main-chain. By using Zn stabilizer, Zn stearate can retard the dehydrochlorination process. However, it was evident (19) that $ZnCl_2$ molecules produced in Scheme 1 could cause a further dehydrochlorination by acting as a catalyst for further PVC degradation, and no longer effectively stabilized

Table 3. Results of hue color index for PVC compounds

Formula	Hue index at various aging time (min)				
	0	30	60	120	270
No stabilizer	2.5YR	0.1YR	9.8R	9.7R	7.7R
Zeolite 2.4 phr	4.5YR	3.0YR	2.8YR	2.7YR	2.4YR
Zn st. 2.4 phr	7.9Y	2.5Y	0.1Y	0.7GY	6.4YR
Pb st. 2.4 phr	8.5Y	5.9Y	5.0Y	4.8Y	9.0YR
Zeolite 4.8 phr	5.5YR	3.0YR	2.4YR	2.3YR	1.4YR
Zn st. 4.8 phr	9.5Y	1.8Y	0.6Y	3.1GY	4.9YR
Pb st. 4.8 phr	9.0Y	4.5Y	4.6Y	3.9Y	0.8Y

Note: Y – Yellow, YR – Yellow-Red, R – Red, and GY – Green-Yellow.

$$—CH=CH—CH—CH_2 \quad + \quad 0.5[Zn(C_{17}H_{35}COO)_2]$$
$$\underset{Cl}{|}$$

$$—CH=CH—CH—CH_2 \quad + \quad 0.5[ZnCl_2] \qquad (a)$$
$$\underset{OOCH_{35}C_{17}}{|}$$

$$Zn(C_{17}H_{35}COO)_2 \quad + \quad 2HCl \longrightarrow ZnCl_2 + 2[C_{17}H_{35}COOH] \quad (b)$$

Sch. 1. Stabilizing mechanism of PVC by Zn stearate.

$$—CH=CH—CH—CH_2 \quad + \quad 0.5[Pb(C_{17}H_{35}COO)_2]$$
$$\underset{Cl}{|}$$

$$—CH=CH—CH—CH_2 \quad + \quad 0.5[PbCl_2] \qquad (a)$$
$$\underset{OOCH_{35}C_{17}}{|}$$

$$Pb(C_{17}H_{35}COO)_2 \quad + \quad HCl \longrightarrow PbCl(C_{17}H_{35}COOH) + HCl \longrightarrow PbCl_2 \quad (b)$$
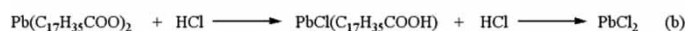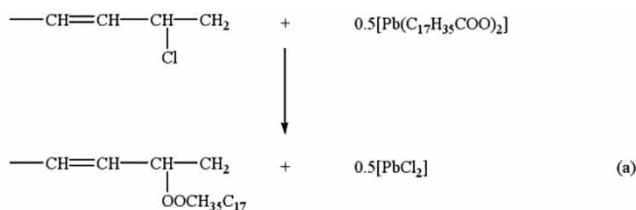
Sch. 2. Stabilizing mechanism of PVC by Pb stearate.

the PVC. This was why the PVC samples turned brown (decreasing of CIE index shown in Figure 1) at longer ageing times of 120 and 270 min. It was observed that the catalytic effect of $ZnCl_2$ molecules to cause the further dehydrochlorination was not seen at shorter ageing times below 120 min, this probably is due to an insufficient concentration of $ZnCl_2$ molecules produced in the PVC compounds (20). It was, however, not intended to quantify the exact concentration of $ZnCl_2$ molecules in this present work. The stabilizing mechanism of PVC by Pb stearate in Scheme 2 was similar to that by Zn stearate, but the releasing rate of HCl molecules by Pb stearate and the further dehydrochlorination reaction by $PbCl_2$ molecules were much slower than those by Zn stearate, and $ZnCl_2$ molecules, respectively (21). Therefore, it could be said that the thermal stabilization of PVC by Pb stearate was more effective than that by Zn stearate.

Figure 2 shows the changes in polyene sequences (ES) for neat PVC compound and wood/PVC composite using the three different thermal stabilizers at dosages of 2.4 and 4.8 phr. The PVC sample with no stabilizers showed the highest polyene content. The results in Figure 2 can be considered in terms of two different effects:

Effect of wood flour incorporation: The concentration of polyene groups increased considerably in the presence of wood flour. The considerable increase in polyene sequence indicates a permanent thermal degradation, resulting from the dehydrochlorination reaction of the PVC in the composite (8, 9). The molecular degradation of PVC by the presence of wood was also observed by Matuana et al. (6, 7). In our work, it was proposed that the PVC degradation induced by the presence of wood particles was probably associated with two production sources, one from moisture residue and the other from HCl release acceleration: (a) moisture residue source; since the wood flour used in this work was hydrophilic in nature, the wood may have picked up moisture during storage, processing and testing. The hydroxyl groups (-OH) in the wood structure result in number of hydrogen bonds between the macromolecules of the wood and polymer. With the presence of moisture, these bonds were broken and new hydrogen bonds with water molecules were formed during the processing, so that Cl atoms could be more easily liberated from the PVC molecules and the HCl gas was then produced (22); (b) HCl release acceleration; it has been proposed that initial HCl and polyene sequences produced during processing could act as a catalyst in the PVC composite to accelerate the rate of the dehydrochlorination reaction, thus producing additional polyene sequences in the composite (23).

Effect of stabilizer type and content: The polyene content decreased in order of zeolite > Zn > Pb stearates, this being the case for both PVC compounds and with wood/PVC composite. The results correspond very well with the CIE yellowness and Hue indexes discussed earlier. It was interesting to note that the stabilizer content for any given stabilizer did not have an effect on the changes in polyene content in the neat PVC, but did have a slight effect in the wood-PVC composite. The difference in polyene content
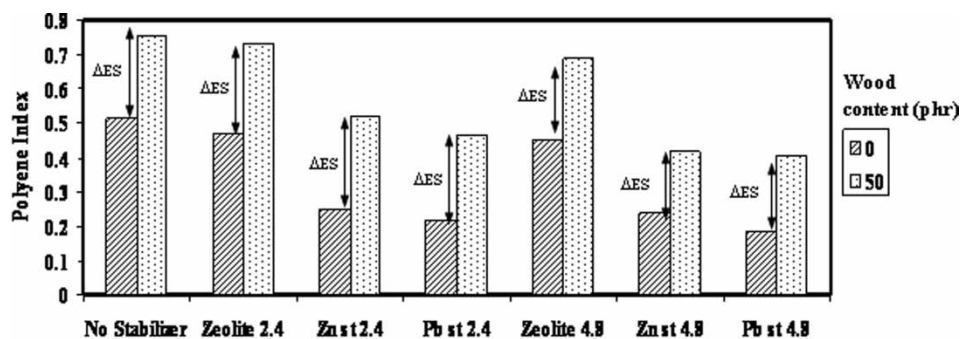
Fig. 2. Polyene sequence of PVC in neat PVC and wood/PVC composite with Zn, Pb and zeolite stabilizers for different ageing times at 177°C.

(ΔES) between unfilled and wood-filled PVC became smaller with increasing the stabilizer dosage from 2.4 to 4.8 phr. This was probably because the stabilizers added into the composites was high enough to reduce the HCl production as discussed in Schemes 1 and 2, and to retard the HCl acceleration as discussed, even in the presence of wood.

Structural changes during the processing of neat PVC and wood/PVC composite could also be assessed by considering percentage weight loss and decomposition temperature change of PVC through the TGA technique. The temperature at which the weight loss occurred directly indicates the commencing point of decomposition of the polymer. The faster the weight loss, the greater the rate of PVC decomposition. Figures 3a and 3b show the plots of %wt loss against temperature for neat PVC compound and with the three different thermal stabilizers at 2.4 and 4.8 phr loadings. It should be noted that the interpretation of the TGA results in Figure 3 cannot be directly compared to that of CIE yellowness or Munsell results in Figure 1 because the TGA results determined the thermal and structural stabilities of PVC around the decomposition temperature of PVC while the CIE and Munsell results evaluated the stabilities of PVC at the test temperature of 177°C under a prolonged period of time. The results in Figures 3a and 3b suggest that the rate of decomposition of PVC with Zn stearate was the fastest, that with Pb ranking second (equal to non-stabilized PVC), and that with zeolite being the slowest. The differences in Zn and Pb stearates on the weight loss change of PVC are due to differences in the abilities of Zn and Pb stearates to retard the dehydrochlorination process, and those of $ZnCl_2$ and $PbCl_2$ molecules to activate the further dehydrochlorination reaction of PVC as discussed earlier. The results in Figures 1 and 3 clearly indicate that Zn and Pb stabilizers could be used to thermally stabilize the PVC at the temperatures below its decomposition temperature, and tended to reduce the decomposition temperature of the PVC. Unlike Zn and Pb stearates, the addition of zeolite into the PVC compound resulted in a considerable shift of decomposition temperature of PVC from 264 to 280°C. The shift of the T_d value indicates a better thermal stability of the PVC. This was because the zeolite is an inorganic substance and can be used to absorb and capture evolved HCl molecules, from the dehydrochlorination reaction, into the zeolite structure (24). This may be why the %wt loss of the zeolite-stabilized PVC did not appear at 264°C (which was referred to as the decomposition temperature of the non-stabilized PVC). However, when the temperature was increased to about 280°C, a sudden drop in %wt loss of PVC added with zeolite was observed, indicating the decomposition temperature of PVC. The considerable shift of decomposition temperature of PVC from 264 to 280°C at this stage can be explained by the saturation of HCl absorption capacity of zeolite (25); the excess HCl evolved from dehydrochlorination reaction could no longer be absorbed by zeolite. The results in this work clearly show that the effectiveness of the three stabilizers used was dependent on the temperature.
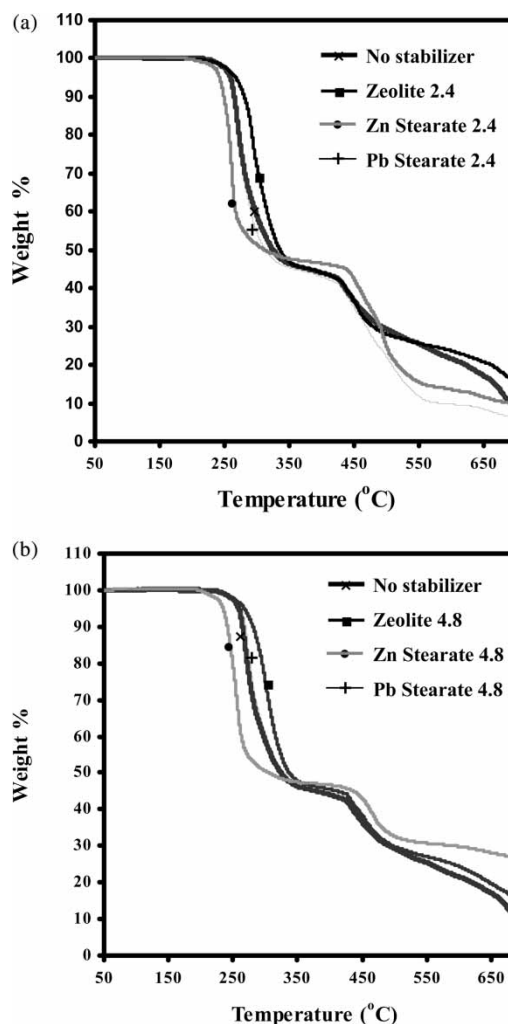
Fig. 3. Plots of weight loss against temperature for neat PVC with Zn, Pb or zeolite stabilizers. (a) 2.4 phr stabilizer loading and (b) 4.8 phr stabilizer loading.

That is, the thermal stabilization of PVC can be referred to as either (a) prolonging the resistance to thermal degradation at service or processing temperatures or (b) increasing the decomposition temperature. In this respect, the Pb stearate was offered for the former case whereas the zeolite was for the latter case.

Figures 4a and 4b show the plots of %wt loss against temperature for wood/PVC composite with the three different thermal stabilizers at 2.4 and 4.8 phr. It can be seen that when adding the wood flour particles into the PVC, the effects of type and content of thermal stabilizers on the weight loss change became insignificant. This suggests that the effect of wood particles had a greater effect on the PVC stabilities than that of the three stabilizers. Table 4 shows the decomposition temperature (T_d) value of PVC in neat PVC and wood/PVC composite using the three different thermal stabilizers with 2.4 and 4.8 phr loadings. As expected, the T_d results corresponded well with the changes
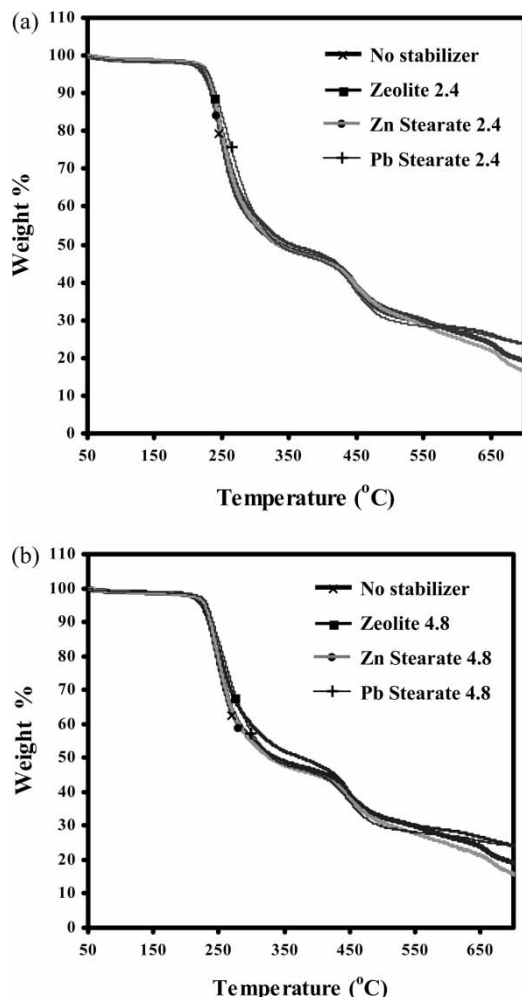
Fig. 4. Plots of weight loss against temperature of PVC in wood/PVC composite with Zn, Pb and zeolite stabilizers. (a) 2.4 phr stabilizer loading and (b) 4.8 phr stabilizer loading.

in %wt loss as shown earlier. For neat PVC compound, the T_d value of Pb stabilized PVC was similar to the non-stabilized PVC ($\sim$264°C), the T_d value reducing to lower values of 248 and 241°C with Zn stearate addition, and shifting to higher T_d

Table 4. Effect of thermal stabilizers and wood particles on decomposition temperatures

Formula	Decomposition temperature (°C) at 10% wt. loss	
	Wood flour of 0 phr	Wood flour of 50 phr
No Stabilizer	264	235
Zeolite 2.4 phr	280	235
Zn Stearate 2.4 phr	248	237
Pb Stearate 2.4 phr	267	241
Zeolite 4.8 phr	280	237
Zn Stearate 4.8 phr	241	237
Pb Stearate 4.8 phr	269	240

value of 280°C with zeolite loading. For wood/PVC composite, the T_d value of PVC in the wood/PVC composite was much lower than that in the neat PVC. The reduction of T_d value by the presence of wood particles is attributed to the presence of moisture in the hydrophilic wood particles, and the HCl releasing acceleration as already discussed. The additions of none of the thermal stabilizers were found to change the T_d value of PVC in the wood/PVC composite.

4   Conclusions

In this work, studies on thermal and structural stabilities of PVC in neat PVC compound and wood/PVC composite were conducted in the presence of wood flour and the additions of Zn and Pb stearates and zeolite as thermal stabilizers. The main findings are noted as follows:

Thermal and structural stabilities of PVC during processing and at the test temperature of 177°C were evaluated through the changes in CIE yellowness and Munsell indices and polyene content. It was found that for neat PVC compound, the additions of Zn and Pb stearates could improve the thermal stabilities of PVC by retarding the upzipping reaction and by reducing the conjugated double bonds in PVC. Pb stearate was found to be the most suitable stabilizer in this work. The incorporation of zeolite was not observed to improve the thermal stability of PVC. For wood/PVC composite, the addition of wood particles resulted in increases in polyene sequences during processing.

Thermal and structural stabilities of PVC around its decomposition temperature range ($\sim$264°C for neat PVC) were evaluated through the changes in %weight loss and T_d value. It was found that for neat PVC compound, the addition of Zn stearate decreased the T_d value whereas that of Pb stearate had no effect on the T_d value. Zeolite was found to act as an acid absorber for PVC thermal stabilization, resulting in a shift of T_d value from 264°C to about 280°C. For wood/PVC composite, loading of 50 phr wood particles in PVC considerably reduced the T_d value of the PVC in the composite from 264 to 235°C. The effect of thermal stabilizers on the changes in T_d result was overruled by the presence of wood particles.

5   Acknowledgments

6   References

1. Kalouskova, R., Novotna, M. and Vymazal, Z. (2004) *Polym. Degrad. Stab.*, **85(2)**, 903–909.

2. Atakul, S., Balköse, D. and Ülkü, S. (2005) *J. Vinyl. Addit. Technol.*, **11(2)**, 47−56.

3. Elakesh, E.O., Hull, R.T., Price, D. and Carty, P. (2005) *Polym. Degrad. Stab.*, **88(1)**, 41−45.

4. Xu, Z.P., Saha, S.K., Braterman, P.S. and Souza, N.D. (2006) *Polym. Degrad. Stab.*, **91(12)**, 3237−3244.

5. Liu, P., Zhu, L., Fang, Y., Zhang, H., Chen, D., Xu, K. and Chen, M. (2007) *Polym. Degrad. Stab.*, **92(3)**, 503−508.

6. Matuana, L.M., Kamdem, D.P. and Zhang, J. (2001) *J. Appl. Polym. Sci.*, **80(11)**, 1943−1950.

7. Matuana, L.M. and Kamdem, D.P. (2002) *Polym. Eng. Sci.*, **42(8)**, 1657−1666.

8. Djidjelli, H., Martinez-Vega, J.J., Farenc, J. and Benachour, D. (2002) *Macromol. Mater. Eng.*, **287(9)**, 611−618.

9. Sombatsompop, N., Chaochanchaikul, K., Phromchirasuk, C. and Thongsang, S. (2003) *Polym. Intl.*, **52(12)**, 1847−1855.

10. Matuana, L.M., Woodhams, R.T., Balatinecz, J.J. and Park, C.B. (1998) *Polym. Compos.*, **19(4)**, 446−455.

11. Sombatsompop, N. and Chaochanchaikul, K. (2005) *J. Appl. Polym. Sci.*, **96(1)**, 213−221.

12. Zhao, Y., Wang, K., Zhu, F., Xue, P. and Jia, M. (2006) *Polym. Degrad. Stab.*, **91(12)**, 2874−2883.

13. Maldas, D. and Kokta, B.V. (1991) *Bio. Technol.*, **35(3)**, 251−261.

14. Sombatsompop, N., Yotinwattanakumtorn, C. and Thongpin, C. (2005) *J. Appl. Polym. Sci.*, **97(2)**, 475−484.

15. Sombatsompop, N., Sungsanit, K. and Thongpin, C. (2004) *Polym. Eng. Sci.*, **44(3)**, 487−495.

16. Ohta, N. and Robertson, A.R. *Colorimetry: Fundamental and Applications*; John Wiley & Sons, Ltd: West Sussex, UK, 92−96, 2006.

17. Steenwijk, J., Langerock, R., Daan, S., Jacco van, H., Geus, J.W. and Jenneskens, L.W. (2006) *Polym. Degrad. Stab.*, **91(1)**, 52−59.

18. Sloane, P. Colour: *Basic Principles New Directions*; Reinhold Book Corporation: New York, 18−21, 1970.

19. Edenbaum, J. *Plastics Additives and Modifiers Handbook*; Van Nostrand Reinhold: New York, 272−337, 1992.

20. Manzoor, W., Yousaf, S.M. and Ahmad, Z. (1996) *Polym. Degrad. Stab.*, **51(3)**, 295−299.

21. Gachter, R., Muller, H. and Klemchuk, P.P. (1990) *Plastics Additives Handbook: Stabilizers, Processing Aids, Colorants for Thermoplastics*; Hansers: Munich, 271−323.

22. Sombatsompop, N. and Chaochanchaikul, K. (2004) *Polym. Intl.*, **53(9)**, 1210−1218.

23. Hjertberg, T. and Sorvik, E.M. In *Thermal Degradation of PVC*, Owen, E.D. (ed.); Elsevier Applied Science: New York, 75−89, 1984.

24. Cruciani, G. (2006) *J. Phys. Chem. Solid*, **67(9−10)**, 1973−1994.

25. Ven, L.V.D., Gemert, V.M.L.M., Batenburg, L.F., Keern, J.J., Gielgens, L.H., Koster, T.P.M. and Fischer, H.R. (2000) *Appl. Clay Sci.*, **17(1−2)**, 25−34.