Palm Oil-Based Compound as Environmentally Friendly Plasticizer for Poly(vinyl chloride)

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Many plasticizers have been invented to serve the purpose of making poly(vinyl chloride) (PVC) into a more flexible plastic. In this work, the potential of palm oil-based compound (Palm1) as a polymeric plasticizer for PVC was investigated. Plasticization of PVC was conducted via the solvent casting technique, using tetrahydrofuran (THF) as the mutual solvent. Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC) were used to find evidence of interactions between the plasticizer and PVC. Transition temperatures (Tgs) of the plasticized PVC were obtained using DSC, and their thermal stabilities were evaluated using a thermogravimetric analyzer (TGA). Results from the study show that the polymeric plasticizer could interact with PVC chains via polar interaction involving –C-Cl of PVC and possibly the -OH groups of Palm1. Tg of the PVC was reduced after it was plasticized with Palm1. The results obtained from this study suggest that the Palm1 may have the potential to serve as an environmentally friendly plasticizer for PVC. J. VINYL ADDIT. TECHNOL., 22:80–87, 2016. © 2014 Society of Plastics Engineers

INTRODUCTION

Poly(vinyl chloride) (PVC) is a type of commodity plastic of great importance, which has been widely used for a variety of industrial and domestic applications. Based on a statistic done by the American Chemistry Council, PVC is the third most widely produced plastic in the United States after polyethylene and polypropylene [1]. It is used in a wide range of products, such as plastic pipes, constructions materials, and consumer goods [2]. PVC by itself is very rigid and may not be suitable for some applications. Thus, it is often plasticized. Diethylhexylphthalate (DEHP) and diisononylphthalate (DINP) are two examples of plasticizers commonly found in plasticized PVC (PVC-P). Although DEHP and DINP could serve as excellent plasticizers to render flexibility to PVC, there are many studies that report the migration of the plasticizers to the surface of the PVC, and subsequently leach out from the plastic. Among the reported cases and studies include the migration of plasticizers out from PVC intravenous bags that are used to hold blood [3, 4], PVC containers [5], food containers, certain food wraps [6], and plastic toys [7].

Migration of plasticizer in PVC is a common phenomenon because plasticizers are attracted to the polymer by weak secondary chemical bonds. These interactions are relatively weak, and, once broken, the mobility of the plasticizers allows them to migrate to the surface of the plastic. The problem may, however, be overcome or reduced by using a polymeric plasticizer that could physically entangle with the polymer and is less mobile. A study that compares the migration resistance between monomeric and polymeric plasticizers was reported by Hakkarainen and Albertsson [8] and the results obtained proved that the latter has higher migration resistance and is better in preserving the material’s properties.

In this work, the potential of palm oil-based compound (Palm1) as a polymeric plasticizer in PVC was investigated. The polar polyfunctional groups, such as –C=O and -OH groups, in Palm1 are expected to yield strong physical interactions with the -CH-Cl of the PVC, thus disrupting the proximity of the PVC chains. Palm stearin is the solid fraction of palm oil, and it was chosen as the source of fatty acids in the synthesis due to economic and technical reasons. Economically, palm stearin is relatively cheaper compared with other commercial oils as it is a byproduct from the production of palm olein. It is always traded at a discounted price [9]. Being the solid fraction of palm oil, palm stearin is made up of high amounts of saturated fatty acids [10]. Absence of a significant amount of -CH=CH- in the system is crucial to avoid crosslinking during the synthesis that could lead to higher transition temperature (Tg) of the final product [11].

Similar to other plasticizers produced from renewable resources, such as epoxidized soybean oil (ESO), Palm1 is also an example of a green product, synthesized using sustainable raw materials, such as palm stearin and glycerol as the main ingredients. Palm1 is, however, expected to perform better in terms of migration resistance owing to its higher molecular weight and long polymeric chain, which could physically entangle with the PVC chain.
Palm1 can be viewed as an oil-modified polyester, where the main chain is made up from polycondensation of phthalic anhydride and glycerol, whereas the fatty acids from palm stearin are grafted as side chains. The presence of these side chains is expected to contribute to more free volume in the plasticized PVC, thus rendering flexibility to the plastic. The current work focuses on the suitability of Palm1 as a plasticizer for PVC in terms of the interactions between the two components, migration resistance, and depression in the $T_g$ of the plastic achieved from the plasticization.

**EXPERIMENTAL**

**Materials**

Refined, bleached, deodorized palm stearin, and glycerol 99.5% were obtained from Emery Oleochemical Malaysia Sendirian Berhad and they were used without further treatment. Fatty acid composition of palm stearin is listed in Table 1 [10]. Phthalic anhydride (PA) was obtained from Merck (Hohenbrunn, Germany), Ca(OH)$_2$ from HmbG Chemicals (Hamburg, Germany), PVC with K value 69 from Sigma Aldrich (Italy), DEHP from MP Biomedical Inc. (Solon, Ohio), acetyl triethyl citrate (ATEC) from Sigma Aldrich (St. Louis, Missouri), and reagent grade tetrahydrofuran (THF) was obtained from Merck (Darmstadt, Germany). All the chemicals involved in this work were used as received.

**Synthesis of Palm1**

Palm1 synthesis began with transesterification process, where 304.4 g of palm stearin (0.34 mol) was allowed to react with 167.1 g of glycerol (1.8 mol) at 230°C for 2 hr. The catalyst used for the transesterification was 0.2 g of Cat(OH)$_2$. The mixture was constantly stirred at 240 rpm using a stainless steel impeller fixed to a digital overhead stirrer throughout the synthesis. The completion of the process was confirmed by conducting solubility test (in alcohol) on the products. The temperature of the system was reduced to $< 150°C$ before adding 256 g of PA (1.73 mol) into the reaction mixture to initiate the polycondensation reaction. Gradually, the temperature was raised back to 230°C and held constant until the acid number of the mixture reached approximately 20 mg KOH/g resin (i.e., <10% of the initial). Presence of some polar groups in the Palm1 is expected to contribute to stronger interaction between Palm1 and PVC. The acid number of the reaction mixture was measured periodically during the synthesis by withdrawing a small amount of reaction mixture from the reaction flask, and dissolved it in neutral solvent (equal volume of isopropanol and toluene), followed by titration using standardized KOH solution in the presence of phenolphthalein as indicator. Throughout the synthesis, water produced during the polycondensation was removed and trapped in customized glassware attached as a sidearm to the reaction flask. It took approximately 8 hr to complete the synthesis. Gel permeation chromatography (GPC) analysis was performed on the product using a GPC instrument (Waters 600) equipped with four styragel columns connected in series and calibrated with monodispersed polystyrene standards.

**Plasticization of Poly(vinyl chloride)**

Plasticization of PVC was carried out via the solvent casting technique using THF as the mutual solvent. PVC solution (10 % w/w of PVC in THF), and Palm1 solution (50 % w/w of Palm1 in THF) were prepared separately at ambient condition. They were then blended together for 6 hr and the temperature of the mixture during the plasticization was maintained at 60°C using a water bath. Codename PVC-P10, PVC-Dhp10, and PVC-Atc10 used in this article represent PVC plasticized with Palm1, DEHP, and ATEC, respectively. The number in the codename represents the weight % of the plasticizers introduced in the formulation. The maximum amount of plasticizer formulated was at 20 wt%, as a higher level led to incompatibility. The blends were cast into films and allowed to dry inside a fume hood for 12 hr. The remainder of the solvent in the film was removed by heating them inside a vacuum oven at 70°C for 96 hr. The same procedures were used to prepare PVC plasticized with commercial plasticizers, DEHP, and ATEC. PVC film without plasticizer (henceforth referred to as u-PVC) was prepared in a similar manner to serve as the control.

**Fourier Transform Infrared and $^1H$-NMR characterizations**

Fourier transform infrared (FTIR) analysis on Palm1 was carried out by casting it into thin film on a KBr cell and scanned on Perkin Elmer RXI FTIR spectrometer. Analyses on dried PVC films were conducted using the same FTIR machine, and each scan was carried out from 400–4000 cm$^{-1}$ at a resolution of 4 cm$^{-1}$. $^1H$-NMR analysis was carried out on Palm1 dissolved in deuterated chloroform (99.8% CDCl$_3$ + 0.03% tetramethylsilane [TMS]) using JEOL JNM-GSX 270 NMR spectrometer. TMS in the chloroform served to lock the signal at 0 ppm.

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Structure</th>
<th>Mean/(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric</td>
<td>CH$_3$(CH$<em>2$)$</em>{10}$COOH</td>
<td>0.2</td>
</tr>
<tr>
<td>Myristic</td>
<td>CH$_3$(CH$<em>2$)$</em>{12}$COOH</td>
<td>1.4</td>
</tr>
<tr>
<td>Palmitic</td>
<td>CH$_3$(CH$<em>2$)$</em>{14}$COOH</td>
<td>59.0</td>
</tr>
<tr>
<td>Palmitoleic</td>
<td>CH$_3$(CH$<em>2$)$</em>{15}$CH=CH(CH$_2$)$_2$COOH</td>
<td>0.5</td>
</tr>
<tr>
<td>Stearic</td>
<td>CH$_3$(CH$<em>2$)$</em>{16}$COOH</td>
<td>4.8</td>
</tr>
<tr>
<td>Oleic</td>
<td>CH$_3$(CH$<em>2$)$</em>{17}$CH=CH(CH$_2$)$_2$COOH</td>
<td>27.4</td>
</tr>
<tr>
<td>Linoleic</td>
<td>CH$_3$(CH$<em>2$)$</em>{18}$CH=CH-CH=CH(CH$_2$)$_2$COOH</td>
<td>7.0</td>
</tr>
<tr>
<td>α-Linolenic</td>
<td>CH$_3$CH$_2$-CH=CH-CH=CH(CH$_2$)$_2$COOH</td>
<td>0.3</td>
</tr>
<tr>
<td>Arachidic</td>
<td>CH$_3$(CH$<em>2$)$</em>{18}$COOH</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Thermal Analysis

Glass T_g of Palm1 and PVC films were measured using differential scanning calorimetry (DSC) (Mettler Toledo 822e), whereas thermogravimetric analyzer (TGA) thermograms were obtained using a TGA 6 (Perkin Elmer). DSC scans were conducted from -60 to 110°C at a heating rate of 20°C/min under N_2 atmosphere. TGA scans were conducted from 50 to 900°C at a heating rate of 10°C/min under N_2 atmosphere. To determine the activation energy of dehydrochlorination of the plasticized PVC, several scans with different heating rates ranging from 10–30°C/min in N_2 were conducted.

Migration Resistance of Plasticizers in Poly(vinyl chloride)

Three plasticized PVC (film thickness = 95 μm), coded as PVC-P20, PVC-Atc20, and PVC-Dhp20 were prepared using 20 wt% of Palm1, ATEC, and DEHP as plasticizers, respectively. The plasticized PVC was cut into square pieces of dimensions of 1 cm × 1 cm before each of them was sandwiched between two u-PVC (dimensions of 1 cm × 1 cm; thickness = 50 μm). They were then heated in a thermal oven at 75°C and pressure 2 atm. The samples were removed from the oven after 1, 2, 4, 6, and 8 days, and the u-PVC films, which have been used to sandwich the plasticized PVC throughout the aging process, were analyzed using FTIR and TGA. Experimental setup used for the migration resistance test is shown in Fig. 1. A similar method was reported in the work by Marcilla et al. [12].

RESULTS AND DISCUSSION

Characterization of Palm1

Figure 2 shows the 1H-NMR spectrum of Palm1, with an inset of its plausible structure. It is a polycondensation polymer that is comprised of glycerol and PA in the main chain, and fatty acids grafted as the side chains. The repeating structure of Palm1 is rather similar to that of DEHP, a common plasticizer for PVC. The resemblance in their structure is an initial indication reflecting the potential of Palm1 as a plasticizer for PVC. Palm1 is an oil-modified polyester with a wide range of molecular weight (MW) and used directly without further purification. Molecular weight of Palm1 recorded from GPC analysis is 3615 g mol⁻¹ with polydispersity index of 1.8. Detailed characterizations on Palm1 and its cooking process have been discussed in earlier publications [11, 13].

Interactions between Palim1 and Poly(vinyl chloride)

The plasticizing effect becomes apparent when the polar groups of the plasticizer interact with the polar groups of PVC, and accommodate the region between the polymer chains. This would effectively provide free volume in the polymer, thus promoting molecular flexibility. It is crucial to have plasticizer-polymer interaction as it affects the extent of the flexibility introduced and retention of the plasticizer in the material. PVC without or with weak plasticizer-polymer interactions often results with only temporary plasticizing effect and is lost over time, causing reversion to the brittle state [14]. Effectiveness of a plasticizer could be judged based on the plasticizer-polymer interaction, and also based on the T_g of the plasticized materials.

The FTIR spectra of Palm1, u-PVC, and PVC-P10 are shown in Fig. 3. The spectrum of PVC-P10 is comprised of peaks from Palm1 and u-PVC. Among the FTIR absorbance peaks from Palm1 that are visible in the spectrum of PVC-P10 include the peak at 3441 cm⁻¹ from -OH stretching, 1727 cm⁻¹ from the A\textsuperscript{C}=O stretching, and 742 cm⁻¹ that corresponds to out-of-plane bending of the orthosubstituted aromatic ring (PA) in the Palm1 chain. A thorough analysis on the spectra revealed that

FIG. 1. Experimental setup of migration resistance test.

FIG. 2. 1H-NMR spectrum of Palm1 with an inset of its plausible structure.
some of the peaks from u-PVC have shifted to a lower wavenumber after it was blended with Palm1 to form PVC-P10. As shown in Fig. 4a, peak at 2974 cm\(^{-1}\), which is one of the characteristic peaks of PVC from the stretching and deformation of C-H of –CHCl [15], is no longer visible in the FTIR spectrum of PVC-P10. The peak could have shifted to a lower wavenumber and merged into a broad peak at 2918 cm\(^{-1}\).

Another significant change observed is shown in Fig. 4b, where the relatively sharp and defined peak at 3500 cm\(^{-1}\) that corresponds to the stretching of free -OH in the Palm1, has become broader and appears at a lower wavenumber, 3441 cm\(^{-1}\) in the FTIR spectrum of PVC-P20. All the changes shown in Fig. 4 originated from either the -OH group of Palm1, or -CHCl of PVC, suggesting that the two components could have interacted with each other via polar interaction. It is noteworthy that the Palm1 in this work was formulated with a slight excess of -OH to avoid premature gelation during the synthesis.

**Transition Temperature of Plasticized Poly(vinyl chloride)**

The effectiveness of Palm1 as plasticizer for PVC is shown in Fig. 5. The \(T_g\) has decreased from 85.3°C in u-PVC, to 66.7°C in PVC-P20. The presence of single \(T_g\) in the DSC thermogram of PVC-P20 reflects the miscibility of Palm1 with PVC. Several endothermic peaks observed in the region 10–30°C correspond to the melting transition of the Palm1. Increasing the amount of Palm1 in the PVC from 5 to 20% w/w has resulted with a decrease in the \(T_g\) due to the increasing plasticizing effect provided by Palm1. The \(T_g\) of plasticized PVC is shown in Fig. 6, along with the \(T_g\) predicted based on the Fox relation [16]:

\[
\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}
\]

where \(w_1\) and \(w_2\) refer to the weight fraction of components in the polymer blend, and \(T_{g1}\) and \(T_{g2}\) refer to the \(T_g\) of the components in the blend. The Fox relation is an extension to the Gordon-Taylor equation, and is usually used to describe the \(T_g\) dependence of polymer blends. As shown in Fig. 6, the \(T_g\)s of Palm1 plasticized-PVC films obtained from DSC analysis agree rather well with those predicted based on the Fox relation. At low levels of Palm1 incorporation, there is a slight negative deviation from the predicted \(T_g\). Palm1, which accommodates the region between the PVC chains could have destroyed the self-association of the chains causing it to have a \(T_g\) lower than those predicted based on the volume additivity of the Fox rule. However, at higher levels of Palm1 incorporation (>10% w/w), increase in the interaction among plasticizers, and chain entanglement between Palm1 and PVC could have resulted with the \(T_g\) slightly higher than those predicted.

**Thermal Stability**

Derivative TGA (dTGA) thermograms of Palm1, u-PVC, and PVC-P20 are shown in Fig. 7. Palm1 has a maximum decomposition temperature of 380°C. However, after it was blended with PVC, the maximum decomposition peak at 380°C is no longer visible in dTGA thermograms of PVC-P20. Instead, the peak at 280°C that corresponds to the maximum decomposition of PVC became broader. The changes observed in the dTGA thermograms of PVC and Palm1 in Fig. 7 suggest that the two could have interacted rather strongly with each other. Such interaction is important to minimize plausible
migration of plasticizer to the surface of the plastic. The Kissinger equation was applied to investigate the thermal stability of the PVC after it was plasticized with Palm1. It is one of the most widely used methods to investigate thermal degradation kinetic parameters, and is expressed as [17]:

$$-\ln \left( \frac{q}{T_p^2} \right) = \frac{E_d}{RT_p} - \ln \left( \frac{AR}{E_d} \right)$$

where q refers to the heating rate, $T_p$ refers to peak temperature at which maximum decomposition occurs, $E_d$ is the activation energy of decomposition, A is the pre-exponential factor, and R is the gas constant.

TGA scans using different heating rates of 10–30°C/min were conducted on u-PVC, PVC-P10, PVC-Dhp10, and PVC-Atc10. The peak temperature where the first decomposition occurs for each sample is listed in Table 2. The table shows that the activation energy of decomposition for PVC-P10 is lower than for u-PVC, indicating a faster degradation rate.

**TABLE 2.** $E_d$ of u-PVC, PVC-P10, PVC-Atc10, and PVC-Dhp10 based on the Kissinger equation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{p10}/K$</th>
<th>$T_{p15}/K$</th>
<th>$T_{p20}/K$</th>
<th>$T_{p25}/K$</th>
<th>$T_{p30}/K$</th>
<th>$E_d$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>u-PVC</td>
<td>563.6</td>
<td>565.0</td>
<td>567.8</td>
<td>572.8</td>
<td>583.3</td>
<td>18.9</td>
</tr>
<tr>
<td>PVC-P10</td>
<td>553.3</td>
<td>563.2</td>
<td>572.8</td>
<td>581.3</td>
<td>589.6</td>
<td>18.9</td>
</tr>
<tr>
<td>PVC-Atc10</td>
<td>552.1</td>
<td>562.9</td>
<td>571.8</td>
<td>581.3</td>
<td>594.7</td>
<td>18.9</td>
</tr>
<tr>
<td>PVC-Dhp10</td>
<td>557.9</td>
<td>569.2</td>
<td>580.7</td>
<td>586.9</td>
<td>72.4</td>
<td></td>
</tr>
</tbody>
</table>

* $T_{p10}$ indicates maximum decomposition temperature at heating rate 10 K min$^{-1}$. 

FIG. 5. DSC thermograms of (a) u-PVC, (b) PVC-P20, and (c) Palm1.

FIG. 6. $T_g$ of Palm1 plasticized-PVC obtained from DSC analysis and Fox relation.

FIG. 7. Derivative TGA thermograms of u-PVC, Palm1, and PVC-P20.
maximum decomposition occurred was taken as $T_p$. Thermal degradation of PVC is a complex phenomenon that involves two stage degradations, starting with dehydrochlorination, followed by decomposition of the resultant polyolefin chains [18, 19]. The gradients from the plot of $-\ln (q/T_p^2)$ against $1000/T_p$ of the plastic films were used to calculate the $E_d$ of dehydrochlorination of PVC and the values are shown in Table 2. PalmI-plasticized PVC has a relatively higher $E_d$ compared to PVC-Dhp10 and PVC-Atc10. Presumably, the strong interaction between PalmI and PVC could have helped in resisting further depreciation of the thermal stability of the plasticized PVC. However, a more detailed study is necessary to investigate the effect of interaction of plasticizer with PVC on the thermal stability of the plastic.

### Migration Resistance of Plasticizers

The FTIR absorbance spectra of u-PVC films, which have been used to sandwich plasticized PVC in the
migration resistance test, are shown in Fig. 8. The peak in the region 1740 cm\(^{-1}\), which corresponds to \(-C\equiv O\) stretching was taken as the peak of interest as all the three plasticizers investigated in this work comprised the \(-C\equiv O\) group. In the event that migration of the plasticizer took place from the plasticized PVC to u-PVC, a peak at 1740 cm\(^{-1}\) would appear in the FTIR spectrum of the u-PVC film. Of the three plasticizers, Palm1 was found to have the best migration resistance as the carbonyl peak in the FTIR spectrum of the u-PVC film starts to become distinct only after 8 days of aging. Although traces of carbonyl peak could be scarcely observed after the sixth day of the test, it was omitted from our discussion as the peak was very weak and insignificant, suggesting minimal, if any, migration had taken place. In the other two systems, distinct carbonyl peak in the FTIR spectra of u-PVC films appeared after 1 day of aging in the PVC-Atc20 system, and 2 days in the PVC-Dhp20 system. Note that the \(-C\equiv O\) peak observed in the FTIR spectrum of u-PVC from the PVC-P20 system is much weaker compared to that from the PVC-Atc20 system, suggesting that a different extent of migration had taken place. A quantitative approach was taken to compare the extent of migration of the plasticizers in the three systems by having the ratio of peak absorbance at 1740 cm\(^{-1}\) to 1330 cm\(^{-1}\) (\(A_{1740}/A_{1330}\)). The FTIR absorbance peak at 1330 cm\(^{-1}\) corresponds to deformation of C–H of \(-CH\equiv Cl\) in PVC. As shown in Fig. 9, migration of Palm1 in the PVC was indeed insignificant compared to the other two.

Figure 10 shows the dTGA thermograms of u-PVC from the three systems. Unplasticized PVC, which was not used for any migration resistance test, served as the control. After 6 days of aging, some changes were observed in the dTGA thermograms of the u-PVC from PVC-Atc20 and PVC-Dhp20 systems. As shown in Fig. 10a, u-PVC films from the two systems show a higher rate of weight loss in the region 150–280°C as compared to the control. The higher rates of weight loss observed are attributed to the plasticizers (ATEC and DEHP) that had migrated to the u-PVC films during the test. In Fig. 10b, a dTGA thermogram of the u-PVC film that had been used to sandwich PVC-P20 for 6 days remained identical to the control, suggesting no Palm1 had migrated to the u-PVC film. Note that the curve in Fig. 10b that corresponds to the u-PVC film after 6 days of the migration resistance test coincides with the control. However, analysis on the u-PVC film from the eighth day of the test shows a slightly higher rate of weight loss at temperatures around 300–380°C due to degradation of Palm1 in the u-PVC film. The results are consistent with the FTIR analysis, in which both showed that migration of Palm1 out from PVC-P20 occurred after 8 days of aging.

CONCLUSIONS

Results from FTIR analyses showed that Palm1 had interacted with PVC after they were blended together. The shifts in the FTIR peaks that correspond to \(-OH\) of Palm1 and \(-CH\equiv Cl\) of PVC suggest that the two components could have interacted with each other via polar interaction involving the two functional groups. The \(T_g\) of the PVC had also decreased as a result of plasticization with Palm1. The \(T_g\) was reduced from 85.3 to 66.7°C at 20% w/w of Palm1 incorporation. The thermal stability of PVC-P with respect to Ed of dehydrochlorination did not
depreciate much and is comparable to neat PVC. As for the migration resistance test, Palm1 proved to have better retention in the PVC as compared to two commercial plasticizers, ATEC and DEHP.

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