

# EFFECT OF MOLECULAR ARCHITECTURE OF PE ON STRUCTURAL CHANGES OF PVC IN PVC/PE MELT-BLEND

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## Abstract

This paper studied the effect of molecular architecture of PE on structural changes of PVC in PVC/PE blends. The thermal property results indicated that PE in the blend between PVC and PE affected the degradation mechanism of PVC. This was explained in terms of a macro-radical cross-recombination reaction between PVC and PE molecules which was confirmed by considering the chemical shift in Carbon-13 Nuclear Magnetic Resonance. The changes in decomposition and glass-transition temperature of PVC in PVC/PE blends were also affected by types and melt flow indexes of the polyethylene.

## Introduction

Poly(vinyl chloride) PVC, is one of the most widely used plastics that can be processed to be both flexible and rigid finished articles. The production of PVC articles in most processes (such as injection moulding and extrusion) generates substantial quantities of scraps which would be likely be re-used or recycled. One of the major problems when recycling or re-using the PVC scraps is thermal degradation. The degradation of PVC is usually proceeded by a dehydrochlorination process which results in the formation of long conjugated double bonds or polyene sequences (-CH=CH-)<sub>n</sub>, thereby causing a color change. The dehydrochlorination process becomes even more rapid in the presence of oxygen, which then results in the formation of carbonyl groups [1]. The polyene sequences formed during the degradation can then lead to cross-linking and chain scissions. The properties of the recycled PVC have been widely studied in literatures [2-4]. Sombatsompop *et al* [5-6] studied the recycling possibilities of various PVC products (pipes and bottles, and cables) in terms of process-abilities, mechanical and thermal properties, and morphological properties as a function of recycled PVC content and types of recyclates.

Overall results indicated that the addition of PVC recyclates strongly affected the rheological, mechanical and thermal properties of PVC products, the optimum content to be added being dependent on the types (which were associated with the initial chemical compositions of PVC compound) and the loading level of PVC recyclates, and UV light [7].

It is widely known that PVC is mostly used in packaging applications such as bottles and blistered products. It is likely used with other types of plastics such as polyethylene. This then makes the recycling more difficult and interesting. Although there have been many researches investigating the structural changes of PVC during the recycling process, only a few studies have reported on the structural change of PVC in PVC/PE blends. It has been confirmed that the presence of PE in PVC affected the structural changes and the degradation mechanism of PVC [8]. Arnold and Mound [9] reported that PVC could degrade faster with the presence of 2% MDPE due to the PE radicals occurring from thermo-mechanical degradation of PE which then consumed thermal stabilizer in PVC.

This paper studied the thermal property changes of PVC in PVC/PE melt blends by considering the effects of PE molecular architecture and content. The blends were characterized using TGA, DMA and <sup>13</sup>C-NMR techniques.

## Experimental

### Raw materials

The polymer matrix used in this study was PVC compound supplied by Thai Plastics and Chemicals Co., Ltd. (Bangkok, Thailand), having a MFI of 5 g/min and a K value of 58. Various grades and MFI values of polyethylenes used, including their suppliers, were listed in Table 1.

## ***Melt blending process***

PVC was melt-blended with various types and contents of PE having two different MFI (5 and 20 g/10min) values using a twin screw extruder (Hakke Polylab-Rheomex, CTW100P, Germany). The concentrations of PE in PVC were varied from 0 to 30 phr. The temperature profile from hopper to three-strand die (each strand having a diameter of 3 mm) was 160/170/210/210 °C and the rotational speed of the screw was set at 120 rpm. The extrudates were then passed through a water bath via the use of a pull-off unit before undergoing a pelletizer to produce blend pellet.

## ***Characterization***

### *Thermal stability*

The decomposition temperature ( $T_d$ ) of the compound was determined using a Perkin-Elmer TGA-7HJ. The temperature was scanned from 50 to 700 °C with a heating rate of 10°C.min<sup>-1</sup> under nitrogen purge. The glass-transition temperature ( $T_g$ ) of the blends was determined using Dynamic Mechanical Analyzer (DMA; Model-2980, supplied by TA Instrument Ltd. (USA). The shape of test sample was rectangular, which had 35 mm long, 12 mm wide, and 2mm thick. The dual cantilever mode of deformation was used under the test temperature ranging from -100 to 150°C, with a heating rate of 3°C.min<sup>-1</sup>, the test amplitude and frequency being 15µm and 1Hz, respectively. The cooling process was achieved through liquid nitrogen. The glass-transition temperature ( $T_g$ ) value was taken from the peak of loss modulus ( $E''$ ).

### *Solid-State <sup>13</sup>C Nuclear Magnetic Resonance*

The <sup>13</sup>C solid-state CP/MAS NMR spectra of the PVC/PE blends, were recorded on a Bruker AVANCE 300 system, operating at 75.4MHz. A zirconia rotor of 7mm diameter was used to acquire the spectra at spinning rates of 4 kHz. The recycle delay and contact times used were 2s and 1ms, respectively. All spectra were accumulated with 2000 scans.

### *SEM investigations*

Failure mechanisms were investigated using a CAM SCAN SEM machine at 15 kV accelerating voltage. The composite fracture surfaces for examination were obtained after two-minute immersion in liquid nitrogen.

## **Results and discussion**

Figures 1a and 1b show the effect of molecular structure of PE on changes in decomposition temperature ( $T_d$ ) of PVC in PVC-PE melt-blends using different types of PE having MFI values of 5 and 20, respectively. Generally, it was found that the  $T_d$  value of PVC increased with the presence of PE, the effect being more pronounced when using the PE with MFI value of 20. However,

increasing PE contents resulted in a progressive decrease in the  $T_d$  to minima, and then the value increased at higher PE contents. It was postulated that there would have been some chemical interaction between PE and PVC occurring during the melt blending process. It has been mentioned by many researchers[10-11] that a macro-radical cross-recombination reaction between PVC and PE radicals could occur during heating and shearing (being referred to as a thermo-mechanical degradation) in the extrusion process, the detail of the macro-radical cross-recombination reaction of PVC and PE being discussed in detail elsewhere[8]. The product from the macro-radical cross-recombination reaction of the PVC and PE was a grafted structure of PVC and PE (which could be written as PE-g-PVC). The formation of the PE-g-PVC structure that occurred during melt-blending can be confirmed through <sup>13</sup>C NMR results as given in Figure 2, which illustrates the chemical shifts of samples of PVC melt-blends having LDPE as a minor phase. The result in Figure 2 indicates that, apart from the chemical shifts of neat PVC (~57 and 44 ppm) and LDPE (~32ppm), there are two additional peaks at chemical shifts around ~26 and ~22ppm, which suggested a structural chemical change in the PVC in the form of PE-g-PVC structure. The resultant PE-g-PVC structure containing in the PVC/PE blends would then lead to an increase in  $T_d$  of the PVC in the blends (at 5 phr PE) since the initial decomposition temperature of PE is usually higher than that of PVC. This postulation could be substantiated using glass-transition temperature results, which will be detailed later on. The decrease in  $T_d$  value with increasing PE content may be caused by a consumption of the thermal stabilizer in PVC by PE radicals which were produced from PE degradation during the extrusion process [9]. The PVC became then more easily to the thermal degradation. Finally, the increase in  $T_d$  value at relatively high content of PE could be as a result of a phase separation of PVC and PE. This view could be re-confirmed using SEM micrographs shown in Figure 3, which illustrates the fractured surface of the PVC/PE samples with 5 and 30phr HDPE contents. It can be seen that the phase separation was obvious for the sample with 30phr HDPE. The phase separation suggested that the flexible chains of PE would no longer attach to the PVC chains, resulting in the increased  $T_d$  of PVC.

Considering the effect of MFI values, it was found that the  $T_d$  value of PVC was higher with more pronounced changes, as a function of PE content in blends, for the sample with higher MFI (lower weight average molecular weight) than those for the sample with lower MFI (higher weight average molecular weight). This could be reasoned by possibility level of the thermal degradation of PE having different molecular weights. That was, the PE with higher MFI value tended to degrade more easily than that with lower MFI value, which allowed the macro-radical cross-recombination reaction between the PVC and PE to be more possible. This view can only be applied for the

HDPE and LLDPE. The effect was found to be opposite for the LDPE, the changes in  $T_d$  being more pronounced when using PE with lower MFI value. This can be explained using the initial  $T_d$  values of these three neat polyethylenes listed in Table 1. It was seen that the  $T_d$  values of the HDPE and LLDPE at the MFI of 5 were higher than those at the MFI of 20, indicating that the degradation became more easily at MFI value of 20. This was not the case for LDPE, the degradation of the LDPE being more susceptible for the LDPE with the MFI of 5.

Figure 4 shows the effect of molecular structure of PE on changes in glass-transition temperature ( $T_g$ ) of PVC in PVC-PE melt blends using PE having MFI values of 5 and 20, respectively. It was observed that the  $T_g$  of the PVC in PVC-PE blends reduced with addition of PE. As the PE content was increased the  $T_g$  gradually increased. It should be noted that the changes in  $T_g$  could be explained through the formation of PE-g-PVC structure from the macro-radical cross-recombination reaction as discussed for the decomposition temperatures. Therefore, the reduction of  $T_g$  of the PVC at the initial PE addition was due to the PE-g-PVC structure, which contained flexible grafted chains of PE on PVC molecules. When increasing the PE contents, the PVC became more susceptible to degradation as a result of the consumed thermal stabilizer. This would give rise to an increase in the number of conjugated double bonds on the PVC chains, which made the PVC chains more rigid, and thus increased glass transition temperatures.

## Conclusion

This paper examined the effect of molecular architecture of PE on structural changes of PVC in PVC/PE blends. The results suggested that a small amount of PE in PVC resulted in a formation of PE-g-PVC structure via macro-radical cross-recombination reaction, which led to an increase in  $T_d$  accompanied by a reduction of  $T_g$  of the PVC in PVC-PE blends. Higher PE concentrations in PVC-PE blends resulted in phase separation between the PE and PVC, and in more susceptible degradation of PVC, that gave a reverse effect on the changes of  $T_d$  and  $T_g$  of PVC in the blends. The changes in  $T_d$  and  $T_g$  were affected by the molecular architecture and molecular weight of PE used in PVC-PE blends.

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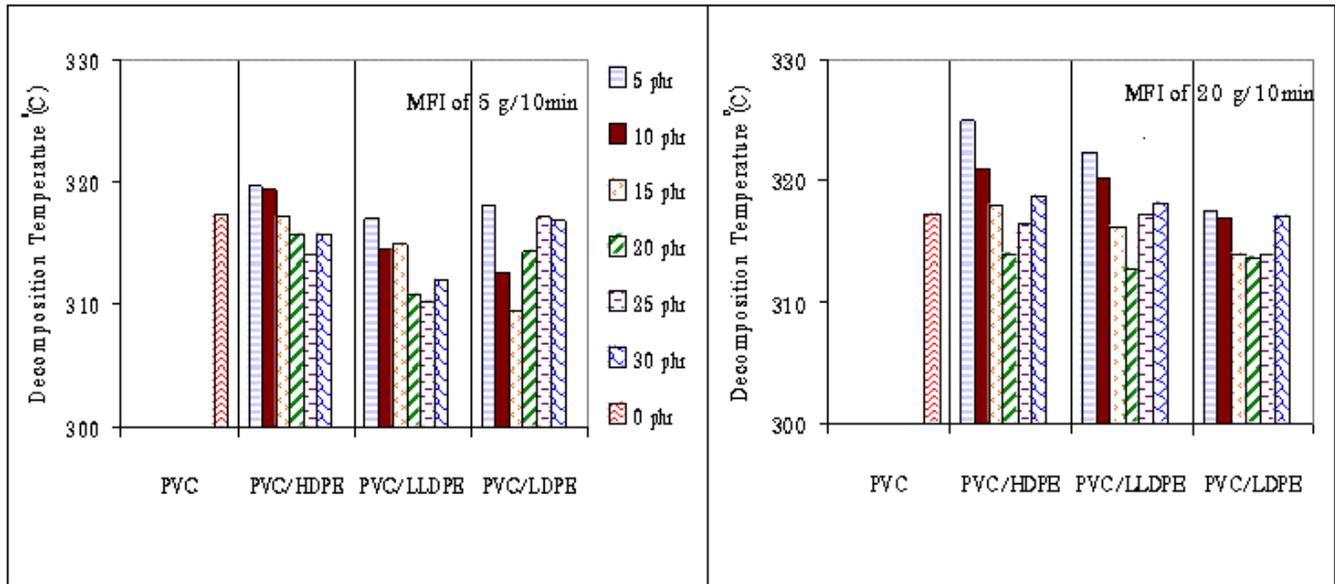
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## Key words

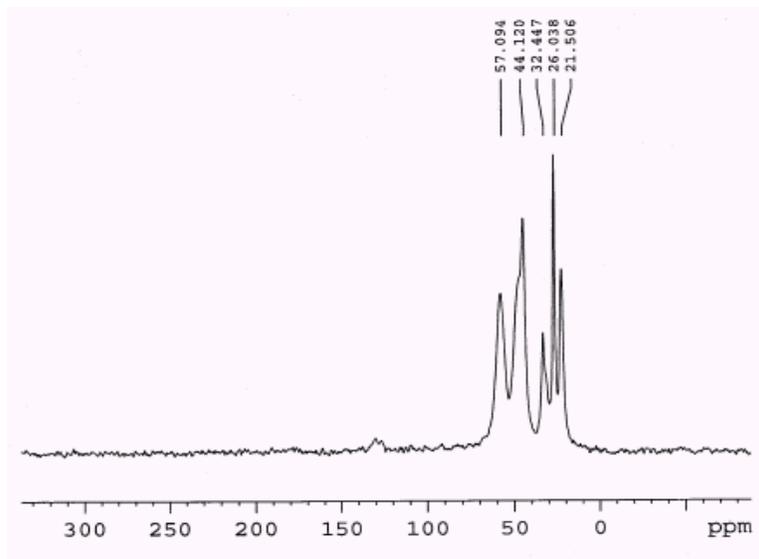
Polyvinyl chloride, thermal degradations, PVC/PE blends, melt blending, extrusion.

**Table1.** Type and MFI value of polyethylenes used in this work.

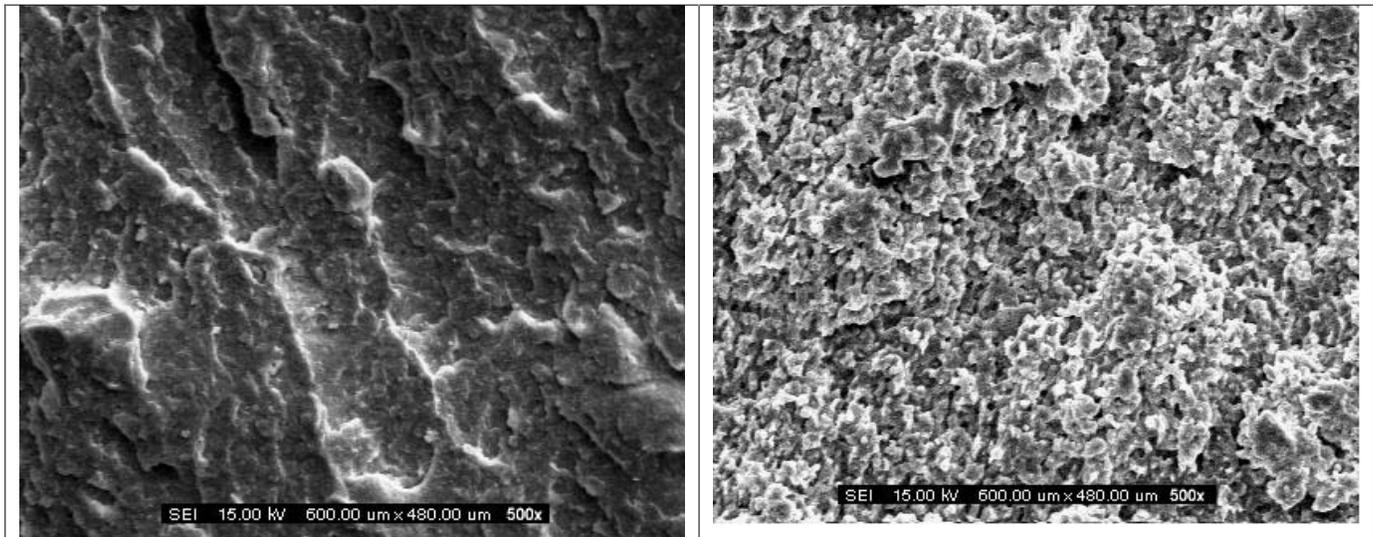
| PE grade        | MFI (g/10 min) | T <sub>d</sub> (°C) | Supplier   |
|-----------------|----------------|---------------------|--|
| LDPE (S1018)    | 20             | 511                 | Thai Petrochemical Industry Public Co., Ltd (Thailand) |
| LDPE (LD1905FA) | 5              | 504                 | Thai Petrochemical Industry Public Co., Ltd (Thailand) |
| LLDPE (M20024)  | 20             | 515                 | Global Connections Co., Ltd. (Thailand)                |
| LLDPE (L1810FI) | 5              | 521                 | Global Connections Co., Ltd. (Thailand)                |
| HDPE (H5818J)   | 20             | 524                 | Thai Polyethylene Co., Ltd. (Thailand)                 |
| HDPE (H68189J)  | 5              | 526                 | Thai Polyethylene Co., Ltd. (Thailand)                 |



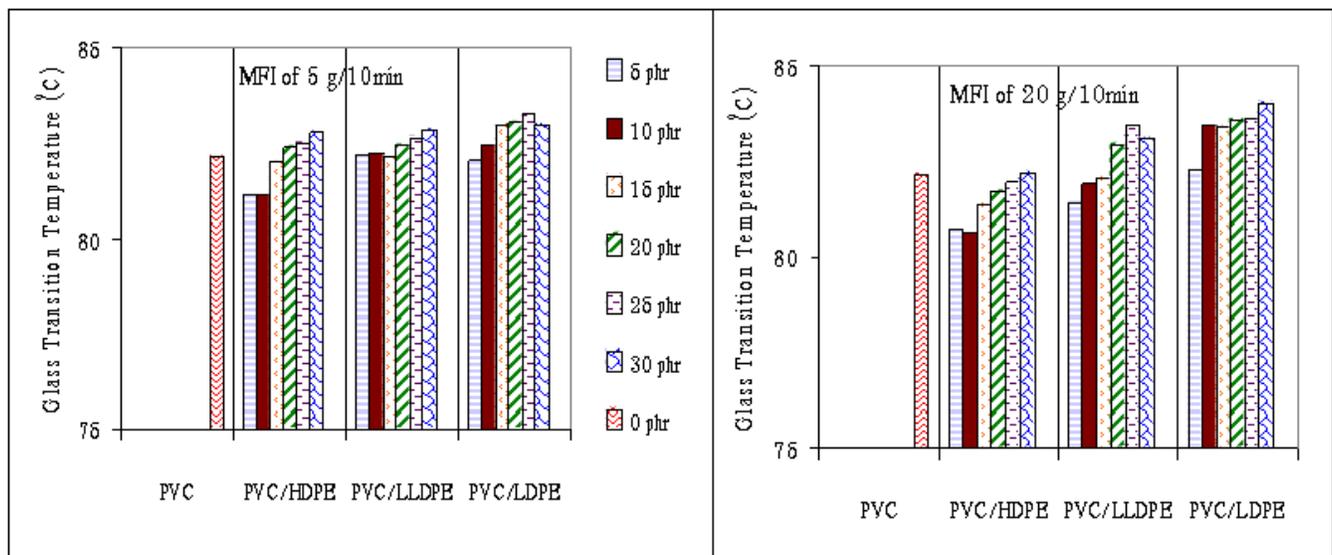
**Figure 1.** Changes in T<sub>d</sub> of PVC in PVC-PE blends for different types and contents of PE



**Figure 2.** <sup>13</sup>C NMR result for PE-g-PVC structure



**Figure 3.** SEM micrographs of PVC blended with HDPE: (a) PVC with 5 phr HDPE, (b) PVC with 30 phr HDPE



**Figure 4.** Changes in  $T_g$  of PVC in PVC-PE blends for different types and contents of PE