ABSTRACT

One of the most serious problems encountered in poly(vinyl chloride) (PVC) processing is due to low thermal stability of the PVC. In this work, the presence of organoclay and low density polyethylene (LDPE) of variable contents were studied in relation to the thermal degradation of PVC. The samples were prepared using an internal mixer with (10, 20 and 30 phr) LDPE and (1, 3, 5 and 7 phr) nanoclay at 180°C and 45 rpm of rotor speed. The morphology of nanoclay was evaluated by X-ray diffraction and transmission electron microscopy. Thermal degradation was tracked by polyene and carbonyl indices using Fourier transform infrared and thermal gravimetric analysis. The results revealed that exfoliation morphology was obtained at 1 and 3 phr concentrations of nanoclay and the intercalation morphology was observed at higher nanoparticle concentration. The addition of LDPE had no significant effect on the dispersion status of nanoparticles. The lowest polyene and carbonyl indices were related to 1 phr concentration of nanoclay. TGA Results showed that the onset temperature of degradation shifted to higher temperature due to the presence of nanoparticles and LDPE and the highest shift was attributed to the sample containing 1 phr of nanoclay and 10 phr of LDPE. Mechanical properties of the samples showed direct correlations with nanoclay and LDPE contents and thermal degradation of PVC. The mechanisms for the prevention of thermal degradation reaction of PVC by LDPE and nanoparticle are proposed and discussed.

INTRODUCTION

In spite of serious environmental and hygienic alerts for PVC, the uses of this polymer in the field of construction (pipes, window frames, etc.), packaging (food, blood bags) and wire coating have attracted much attention. Although having favourable properties, such as non-flammability, low cost and formulating versatility, the low thermal stability of PVC is considered as one of the most serious industrial problems [1-3]. The degradation of PVC has been widely studied since 1940. Most of the early research works have been focused on the dehydrochlorination reactions to improve the thermal stability of PVC [4,5]. The overall experimental results have led to the discovery of new heat stabilizers. In further research works the
kinetics of thermal degradation and decomposition products have been studied [6].

Today, the thermal degradation mechanism of PVC is established. The main process involved in thermal degradation of PVC is known to be dehydrochlorination. The onset temperature of PVC dehydrochlorination is around 100°C which due to the formation of long conjugated double bonds or polyene sequences a process of discoloration develops. The rate of this process becomes even more rapid in presence of oxygen and HCl, which results in formation of carbonyl groups, as reaction catalyst which autocatalyzes accelerating reactions. In order to process PVC with minimum extent of thermal degradation, a number of chemical combinations, such as lead compounds, organotin compounds and those of other metals can be used as stabilizers [5,7].

In addition to the above heat stabilizers, incorporation of polyethylene into PVC compounds has been reported to prevent PVC degradation. Thongpin et al. [8] studied the degradation behaviour of PVC/PE blend in terms of decomposition temperature, polyene index and glass transition temperature. They concluded that the addition of small amount of PE could thermally stabilize the PVC molecular structure. Effects of molecular architecture of PE and the compatibilizers on thermal and rheological properties of PE/PVC blend have been reported in 2001-2004 [9-11]. It should be noted that PE and PVC are immiscible with very low adhesion strength between the two phases which gives rise to poor mechanical properties. Using chlorinated polyethylene, methyl methacrylate-butyl acrylate copolymer, butadiene-block-(styrene-co-acrylonitrile), poly(ethylene-co-methacrylate), butadiene rubber solid phase dispersant as compatibilizers have been reported [12-14].

In recent years, the prospect of developing PVC nanocomposites with significantly improved properties has attracted much attention. In this respect, PVC/cellulose whiskers [15], PVC/nano-CaCO₃ [16] and PVC/organoclay [17-21] have been studied.

The effect of nanoclay on thermal properties of PVC was evaluated by Wang et al. using thermal gravimetric analysis, indicating that the clay had an effect on the course of PVC degradation [22]. However, some reports state that PVC/organoclay nanocomposite is less thermally stable than PVC itself [23].

The present study is motivated by the current interest on nanoclay influence on thermal degradation of PVC. As a new approach, an attempt has been made to study the effects of LDPE and silicate layer nanoparticles on the thermal degradation of PVC. Polyene and carbonyl indices were evaluated using Fourier transform infrared spectroscopy (FTIR) and the nanocomposites were thermally characterized using thermogravimetric analysis (TGA). The morphology of the blend and nanoparticles were determined by XRD, TEM and SEM and their morphological features have been studied in relation to the thermal degradation of PVC compound. In addition, mechanical properties (Young's modulus and impact resistance) were studied in details.

**EXPERIMENTAL**

**Materials**

The polymeric materials in this study were: suspension grade PVC (k-value 65) with S6558 trade name, from Bandar Imam Petrochemical Co. (Iran); LDPE with LF0200 trade name (MFI 2 g/10 min) from Bandar Imam Petrochemical Co. (Iran); chlorinated polyethylene (CPE) with trade name Tyrin 7100 from Dow Co. (USA). The PVC compound was composed of 0.8 phr calcium stearate, 1.5 phr tetrabasic lead sulphate and 0.2 phr PE wax, purchased from local market.

The nanoclay was Cloisite® 30B from Southern Clay Co. (USA) with 1.85 nm initial gallery heights, modified with methyl, tallow, bis-2-hydroxyethyl quaternary ammonium and cation exchange capacity (CEC) was 90 mequiv/100 g.

The PVC powder and other ingredients of the formulation were dry blended in a turbomixer (Papenmeier Co., Germany) at 110°C and 1000 rpm for 8 min. The PVC compounds were comprised of three levels of LDPE (10, 20 and 30 phr) and four levels of nanoclay (1, 3, 5 and 7 phr) as given in Table 1. The compounding was carried out using an internal mixer (Brabender 90, USA) with a cam blade at 180°C and 45 rpm of rotor speed for 5 min.
The obtained compounds were cooled at room temperature and the specimens for the tests were produced using compression moulding machine WCH202, Toyseiki, Japan at 180°C and 160 kg/cm² pressure.

**Characterization**

XRD Measurements were carried out at room temperature using an X,pert Philips diffractometer, The Netherlands. X-Ray diffractometer with CuKα = 1.541 nm with a generator voltage of 40 kV and a generator current of 50 mA. The scanning rate was 1º/min over a range of 1-10. The morphology structure of the nanocomposites was investigated by an EM 208 Philips, transmission electron microscope, The Netherlands, with an acceleration voltage of 100 kV. The ultrathin slides were obtained by an Ultracut UCT, Leica, Germany, at room temperature.

To study the microstructure of PVC/LDPE blend, a Philips scanning electron microscopy, XL30, The Netherlands, was employed to study the cryogenically fractured surface.

Tensile test (according to ASTM D638) was carried out using a universal testing machine (Gotech, Taiwan) at crosshead speed of 5 mm/min. Impact strength (according to ASTM D256) was measured on notched samples using a Zwick Model 5102 instrument, Germany.

To determine the polyene and carbonyl index, the FTIR spectroscopy was performed on the samples using Equinox55 FTIR spectrometer to obtain the spectra of absorbance against wavenumber. The films were prepared by compression moulding at 190°C for 2 min. Polyene and carbonyl indices were calculated according to:

\[
\text{Polyene index} = \frac{T_B - T_{1579}}{T_B - T_{2916}}
\]

\[
\text{Carbonyl index} = \frac{T_B - T_{1720}}{T_B - T_{2916}}
\]

where \(T_{2916}\), \(T_{1720}\) and \(T_{1579}\) are related to carbon-hydrogen, carbonyl bonds and C=C bonds, respectively. \(T_B\) is the base line of the FTIR spectrum and it is usually equal 1.

TGA was accomplished using TGA-7HT from Perkin & Elmer (USA) in the range of 30-600°C with 10°C/min under the nitrogen atmosphere.

### Table 1. Formulation of the samples.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>PVC Compound (phr)</th>
<th>LDPE (phr)</th>
<th>Chlorinated PE (phr)</th>
<th>Nanoclay (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P100/LD10/N0</td>
<td>100</td>
<td>10</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>P100/LD10/N1</td>
<td>100</td>
<td>10</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>P100/LD10/N3</td>
<td>100</td>
<td>10</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>P100/LD10/N5</td>
<td>100</td>
<td>10</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>P100/LD10/N7</td>
<td>100</td>
<td>10</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>P100/LD20/N0</td>
<td>100</td>
<td>20</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>P100/LD20/N1</td>
<td>100</td>
<td>20</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>P100/LD20/N3</td>
<td>100</td>
<td>20</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>P100/LD20/N5</td>
<td>100</td>
<td>20</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>P100/LD20/N7</td>
<td>100</td>
<td>20</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>P100/LD30/N0</td>
<td>100</td>
<td>30</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>P100/LD30/N1</td>
<td>100</td>
<td>30</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>P100/LD30/N3</td>
<td>100</td>
<td>30</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>P100/LD30/N5</td>
<td>100</td>
<td>30</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>P100/LD30/N7</td>
<td>100</td>
<td>30</td>
<td>10</td>
<td>7</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

In order to interpret the effect of nanoclay on thermal degradation of PVC, it is useful to start by expressing the morphology of nanocomposite. Figure 1 shows the XRD diffraction pattern of neat organoclay (Cloisite® 30B) and PVC/LDPE blend ratio: 100/10 containing different organoclay concentrations. The diffraction peak of organoclay at 2θ = 4.38° corresponds to 1.85 nm inter-gallery distance (d_{001}). For samples containing 1 and 3 phr of nanoclay the diffraction peak at 2θ = 4.38° disappeared, indicating the formation of exfoliated structure in composite samples. By addition of nanoclay at higher contents (5 and 7 phr), diffraction peaks of organoclay were lowered by formation of intercalated structure in these nanocomposite samples. Diffraction peaks of samples containing 5 and 7 phr nanoclay were observed at 2θ = 2.21° (d_{001} = 3.2 nm) and 1.96 and 2.69° (d_{001} = 3.82 nm and 2.55 nm), respectively. It seems that matching between the polarity of PVC and Cloisite® 30B facilitates the diffusion of polymeric chain into the layers of the nanoclay contributing to exfoliation state. Addition of nanoclay in samples results in nanoclay agglomeration which as a consequence leads to an intercalated morphology. The morphology of nanocomposite samples in relation to polyethylene concentration is demonstrated in Figure 2, where the XRD pattern of samples containing 3 phr nanoclay with different polyethylene contents (10, 20 and 30 phr) and neat nanoclay is shown. As mentioned earlier, the diffraction peak of Cloisite® 30B is observed at 2θ = 4.38°. By addition of polyethylene no morphological changes were observed and the samples showed exfoliated morphology similar to sample of polyethylene with 10 phr content. The main reason for this trend may be attributed to location of nanoclay in PVC phase. Since both PVC and nanoclay are polar (in contrast to LDPE), nanoclay is located in PVC phase. In other words, the increase of the LDPE phase in the blend did not affect the morphology of the nanocomposite because nanoparticles are mostly dispersed in PVC. Evaluations of nanoparticles distribution in different phases of the blend have been reported in literature [24-26].

In order to have a better insight on the morphology of nanoparticles, TEM test was applied on samples. Micrographs of sample P100/LD10/N3 in low and high magnifications are shown in Figure 3. This figure shows delaminated and dispersed layers while the stacks of nanoclay layers are observed in some regions. The dark lines represent the intersection of nanosilicate layers while white background corresponds to blend matrix. Therefore the TEM and XRD analyses show the typical morphology of the nanocomposite consisting of mixed dispersed individual layers as well as the stacks of platelets.

The SEM micrographs of the blends with different concentrations of LDPE (10 and 30 phr) are illustrated in Figure 4. It may be observed that the predominant morphology is droplet-matrix and the LDPE as minor phase is dispersed in PVC matrix,
and it seems the state of morphology is not affected by the presence of nanoparticles, because nanoclay is located in PVC phase and not in LDPE domains. Due to compatibilizing effect of CPE in LDPE and PVC blend system in the compound, the fractured surfaces were fine.

The typical FTIR spectrum and polyene index of samples at different nanoclay concentrations are shown in Figure 5. The absorbance at 1579 cm\(^{-1}\) implying the formation of C=C bonds gives a polyene index value based on its band intensity. It is clear that, the polyene index is affected by the presence of nanoclay with a decremental trend. The greatest decrement is related to the samples containing 1phr nanoclay whereas the samples containing 3, 5 and 7 phr nanoclay showed higher decremental values. This behaviour can be explained as follows: during
the PVC processing, thermal degradation occurs and the macroradicals form. There are three sources for trapping the macroradicals and preventing the formation of double-bonds: LDPE, heat stabilizers and nanoparticles. The absorption mechanism of the macroradical by LDPE has been reported by Thongpin et al. [8] and Sombatsompop et al. [9]. They explained that PVC macroradicals produced from a dehydrochlorination reaction during the melting process have promoted the degradation of long-chain polyethylene and probably have led to hydrogen abstraction from polyethylene molecules. The polyethylene macroradicals subsequently must have undergone chain scission, producing shorter-chain PE molecules in the blend. In that case, the dehydrochlorination of PVC would have had less chance to occur, and thus more stabilized PVC molecules exist in the mixture.

The existence of OH group in the modifiers of nanoclay can also help to absorb PVC macroradicals. In exfoliation states, these groups are more available and the possibility of the reaction with macroradicals is higher than that of intercalated morphology. Thus, with exfoliated morphology fewer double-bonds (1 and 3 phr) are formed and the minimum polyene indices are obtained.

As it is evident in Figure 5, polyene index is decreased with higher polyethylene up to 20 phr, where it is then increased. This behaviour is mainly due to the quantity of heat stabilizer being consumed by LDPE macroradical at its highest concentration. The similar result has been reported by Thongpin and Sombatsompop et al. [8,9].

Figure 6 shows the carbonyl index of samples and a typical FTIR spectrum which shows the absorbance at 1729 cm$^{-1}$. This peak is an indication of reaction between PVC macroradicals and oxygen. In neat PVC, heat stabilizers only inhibit oxidation reactions and the carbonyl index of macroradicals remains at its maximum value. By addition of LDPE and nanoclay to a compound, the carbonyl index was decreased. Similarly the minimum amounts were also related to 1 and 3 phr of nanoclay. Figure 7 shows the probable reactions for PVC macroradicals which inhibit the oxidation reaction via reaction with OH groups of nanoclay surfactant and LDPE chains. In both reactions, the macroradicals abstract hydrogen from OH groups or LDPE chains and hence they are...
stabilized. There are different ways for new radicals to be produced which are given by numbers 1 to 3 in Figure 7. All of these reactions occur between two radicals with products in stable form. The higher polyene and carbonyl indices of nanocomposites with increased Cloisite® 30B content up to 1 phr may result from the influence of ammonium salt. It is known that thermal decomposition of quarternary ammonium salt could take place on the basis of Hofmann degradation mechanism. Hofmann degradation of the ammonium salts is accompanied by formation of H+ and HCl. The existence of H+ and trace HCl may catalyze and accelerate the dehydrochlorination of the PVC chains [27].

**Figure 7.** Probable reactions for PVC macroradicals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset temperature (°C)</th>
<th>The temperature of highest rapidity (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>283.0</td>
<td>449.5</td>
</tr>
<tr>
<td>P100/L10/N0</td>
<td>296.7</td>
<td>464.6</td>
</tr>
<tr>
<td>P100/L10/N1</td>
<td>301.0</td>
<td>471.4</td>
</tr>
<tr>
<td>P100/L10/N3</td>
<td>286.4</td>
<td>481.0</td>
</tr>
<tr>
<td>P100/L10/N5</td>
<td>287.1</td>
<td>475.8</td>
</tr>
<tr>
<td>P100/L10/N7</td>
<td>287.0</td>
<td>473.6</td>
</tr>
<tr>
<td>P100/L20/N3</td>
<td>298.0</td>
<td>480.0</td>
</tr>
<tr>
<td>P100/L30/N3</td>
<td>292.0</td>
<td>480.0</td>
</tr>
<tr>
<td>Cloisite® 30B</td>
<td>298.0</td>
<td>427.0</td>
</tr>
</tbody>
</table>
The thermal behaviour of samples with different nanoclay contents in TGA test are demonstrated in Figure 8 and the data including onset temperature and most rapid decomposition temperature are presented in Table 2. It is clear that by addition of LDPE and nanoparticles, the onset and most rapid temperature of decomposition have been shifted to higher values. The highest shift for onset temperature of decomposition was attributed to the sample containing 1 phr of nanoclay and 10 phr of LDPE. It is interesting to note that the maximum onset temperature belongs to the samples (301°C) whereas the onset temperature of Cloisite® 30B is 298°C. In other words, by the start of the decomposition of nanosurfactant at 298°C some parts of macroradical transition (as the main deactivation process of PVC macroradicals) are disturbed.

The mechanical properties of the samples were
determined to correlate the effect of nanoclay, LDPE concentration on thermal degradation of PVC. The dependency of the Young's modulus and impact resistance of samples on nanoclay concentration is demonstrated in Figure 9. Due to lower modulus of LDPE, by its further increase it would lead to lower Young's modulus. The enhancement of modulus with incorporation of nanoclay to polymeric system has been reported in literature and our result shows a similar trend as well. It seems that the effect of nanoclay by preventing the thermal degradation would not have any enhanced effect on Young's modulus.

The maximum impact resistance was obtained in samples containing 3 phr of nanoclay because of exfoliation morphology. Favourable dispersion of nanoparticles leads to easier stress transfer from the matrix to particles and so higher energy would be needed for composite to fracture.
This article addresses some key issues related to improvement of thermal stability of PVC by incorporation of LDPE and nanoclay. The PVC compounds containing LDPE and nanoclay of different concentrations were prepared and their thermal stability was evaluated by polyene and carbonyl index using TGA. Some results are summarized as below:

- The exfoliated morphology of nanoparticles was observed in samples containing 1 and 3 phr nanoclay and intercalated morphology was obtained at higher concentration of nanoclay (5 and 7 phr).
- The nanoclay morphology remained intact at higher LDPE concentration because of the location of nanoclay in the PVC phase.
- Polyene and carbonyl indices dropped with incorporation of LDPE and nanoclay. However, the greatest decrement for these indices were related to lower quantities of nanoclay due to fully exfoliated morphology.
- The onset of decomposition temperatures was raised in presence of nanoclay and LDPE due to trapping of macroradicals. The highest shift for onset temperature of decomposition was attributed to 1 phr nanoclay and 10 phr LDPE contents.
- The maximum impact resistance was obtained in samples containing 3 phr nanoclay because of exfoliated morphology.
- Reaction between PVC macroradicals and nanoclay surfactant results in formation of more stable macroradicals.

REFERENCES

3530, 2008.


