4

Effect of additives on rheological properties of PHB

Rheology considers the response of a material to deformation. It involves the relations between the amount of deformation and the force that produces the deformation. Such relation are called the rheological properties. Rheology is most often used with regard to materials in the liquid state and the material flow. Polymer melts are characterized by a viscosity which depends on the shear rate. In rheology the melt index and the viscosity using capillary viscometers or a rotational rheometer are measured. The shear viscosity is defined as the ratio of shear stress to the shear rate under test conditions:

\[ \eta = \frac{\text{shear stress}(\tau)}{\text{shear rate}(\dot{\gamma})} \text{[Pa.s]} \]

4.1. Experimental methods

4.1.1 Capillary rheometer

A capillary rheometer (Götffert Rheograph 2002) was used for steady shear measurements and the viscosity was determined at shear rates of 10 to 1000 s\(^{-1}\).

The principle of operation of a capillary rheometer is the determination of the relationships between pressured drop and the flow rate. Capillary rheometers are widely used instruments for the determination of the viscosity of melts. In the case of melts the flow is generated by either forcing a piston to move through a reservoir at constant speed or by applied pressure. Molten polymers are non-Newtonian fluids and the viscosity is evaluated as a function of shear rate

4.1.2 Oscillatory rheometer

The linear viscoelastic shear properties of PHB and its blends were measured in the molten state with a parallel plate type Weissenberg rheometer (see figure 4.1). The plates of the rheometer have a diameter of 40 mm.

The storage modulus measures the elastics response of a polymer and the loss modulus the energy dissipated during flow deformation. A Frequency sweeps from 0.01 rad s\(^{-1}\) to 200 rad s\(^{-1}\) at different temperatures from 170°C to 210°C were used. The results are reported in the
form of plots of the storage and loss modules $G'(\omega)$, $G''(\omega)$ or viscosity $\eta^*(\omega)$ as a function of frequency.

4.1.3 The Melt flow index (MFI)

The melt flow index is used to characterize a polymer melt and as a quality control test. It is a single point measurement using a standard test condition. The flow rate is determined as a function of applied load. Melt flow index (MFI) is the mass flow rate expressed in grammes per 10 minutes. Extrusion takes place isothermally in 10 min under constant temperature through a die of standard size. The sample of 5 g as a powder or a pellet is heated for 5 minutes in the barrel and extruded through the die under a constant load of 2.16 kg. The melt flow index (see table 8) for PHB and its blends was measured at various temperatures (170, 180 and 190°C).

Table 9: MFI values for PHB and its blends.

<table>
<thead>
<tr>
<th></th>
<th>MFI value at 170 °C</th>
<th>MFI value at 180 °C</th>
<th>MFI value at 190 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/10 min</td>
<td>g/10 min</td>
<td>g/10 min</td>
</tr>
<tr>
<td>PHB</td>
<td>0.06</td>
<td>0.11</td>
<td>0.5</td>
</tr>
<tr>
<td>Blend 10</td>
<td>2</td>
<td>7.52</td>
<td>14.93</td>
</tr>
</tbody>
</table>

4.2 Viscoelastic properties
The distribution of relaxation times and relevant material parameters were determined to obtain more information about the flow process. It is possible to calculate the stress components resulting from a shear type of deformation using the Boltzmann superposition principle given as:

$$\tau(t) = \int_{-\infty}^{t} G(t-t')\gamma'(t')dt'$$  \hspace{1cm} (1)

Where $\tau$ is the shear stress, $G(t)$ is the linear relaxation modulus, and $\gamma'$ is the shear rate. To describe the linear viscoelastic behavior of polymer melt, the Maxwell model is used:

$$G(t-t') = \sum_{i=1}^{N} G_i \exp \left[-(t-t')/\lambda_i\right]$$  \hspace{1cm} (2)

Polymer melts are non-Newtonian fluids, therefore modules and viscosity are functions of the shear rate of the circle-frequency.

The relaxation behavior of polymer molten is described not with a relaxation time but with a relaxation time spectrum ($\lambda_i$) and a spectrum of the relaxation strength ($g_i$). The Maxwell model results in the following frequency dependency of $G'$ and $G''$:

$$G'(\omega_i) = \sum_{i=1}^{N} G_i \frac{(\omega \lambda_i)^2}{1+(\omega \lambda_i)^2}$$  \hspace{1cm} (3)

$$G''(\omega_i) = \sum_{i=1}^{N} G_i \frac{\omega \lambda_i}{1+(\omega \lambda_i)^2}$$  \hspace{1cm} (4)

$$|G^*(\omega)| = \left[G'(\omega)^2 + G''(\omega)^2\right]^{1/2}$$  \hspace{1cm} (5)

Where $G_i$ is the relaxation strength, $G'$ is storage modulus, $G''$ is loss modulus, the magnitude of $G^*$ is the complex modulus and $\lambda_i$ is the relaxation time.

4.3 Results and discussions

4.3.1 Rheological studies

The rheological characterisation of PHB and its blends is performed using a capillary and a oscillatory rheometer. Figure (4.2 A) shows the isothermal viscosity of the blend 10 as a function of frequency. Increasing the temperature from 170°C to 210°C leads to a change in the viscosity to lower values. Figure (4.2 B) shows the storage and loss moduli of the blend 10 as a function of frequency at different temperatures of melt processing. The thermal instability affects the viscosity and modules, especially at high temperature melt processing. By increasing the frequency, the modulus of the blend 10 increases. Figure (4.3 A) shows the
viscosity versus steady shear rate at different temperatures of melt processing 170°C, 175°C and 180°C. An increase in the shear rate decreases the viscosity. Figure (4.3 B) shows by applying the Cox-Merz rule [127] that the complex viscosity is related to the viscosity in steady shear, i.e., \( \eta(\gamma') = \eta^*(\omega) \bigg|_{\gamma'=\omega} \). where \( \eta(\gamma') \) is the shear rate dependent viscosity, with \( \gamma' \) as the steady state shear rate. \( \eta^*(\omega) \) is the absolute value of the frequency-dependent complex viscosity derived from dynamic oscillatory experiments, with frequency \( \omega \) in radians per second. Utracki and Schlund et al. [128] suggested that \( \eta(\gamma') = \eta^*(\omega) \) for miscible blends.

### 4.3.2 Activation energy \((E_a)\) values after cooling by various temperatures melt processing

The viscosity of the melt depends on the processing temperature \((T_{tmp})\) with an increase in \((T_{tmp})\) decreases the viscosity. The flow activation energy is one of the most important molecular parameters and provides information on the structure flow of the polymers. Figures (4.4 A, B) show the viscosity, plotted against \(1/T \) (K\(^{-1}\)). A straight line with a positive slope is obtained. This is called an Arrhenius plot; the slope of this plot gives the flow activation energy \((E_a)\). The mathematical expression for the Arrhenius plot is:

\[
\ln \frac{\eta}{\eta_0} = \frac{E_a}{R} T^{-1}
\]

For various polymers, the value of \(E_a\) lies between 15 and 120 kJ/mol. Figure (4.5A) shows that the value of activation energy of blend 10 was 10 kJ/ mol when cooled after a melt processing at 175°C. It increases with a more intensity temperature process and has the value of 59 kJ / mol when cooled after melt processing at 210°C. It is well known that branching reactions occur at higher temperatures; this leads to an increase in the rotational restrictions along the chain backbone and a higher value of activation energy. By increasing the temperature from 190°C to 200°C, the value of activation energy of PHB decreases from 24.36 to 12.66 kJ/mol (see figure (4.5 B)). The complex viscosity \(\eta^*\) is defined as \(\eta^* = \eta^\prime - \eta^\prime\prime\) and \(\eta^* = G^*(\omega)/\omega\). The material parameters can be calculated from the relaxation properties like zero shear viscosity

\[
\eta_0 = \sum_i G_i \lambda_i, \text{ elastic coefficient } J_\varepsilon = \frac{\sum G'(\omega)}{\omega^2} = \sum G\lambda^2_i, \text{ the equilibrium compliance}
\]

\[
J_\varepsilon^0 = \frac{\sum G'(\omega)}{G''(\omega)} = \frac{\sum G_i \lambda^2_i}{(G\lambda_i)^2}, \text{ Retardation time } \lambda = \eta_0 J_\varepsilon^0 = \frac{\sum G_i \lambda^2_i}{\sum G\lambda_i}
\]

Where the \(G_i\) are the relaxation strengths and \(\lambda_i\) the relaxation time.

Figure (4.6 A) shows for blend 10 the discrete relaxation time spectrum calculated with Nrleg program for different temperatures 170°C, 190°C and 210°C from the measured modulus \(G'(\omega)\) and \(G''(\omega)\). The result is \(\eta_0 = 3.2 \text{ Pas}, J_\varepsilon = 2.9, J_0 = 4.9 \text{ Pa}^{-1}, \lambda = 3.2^4.9 = 15.9 \text{ s. PHB melts at higher temperatures immediately as a thin honey-like liquid, because the polymer is}\n
without any branching. It is linear; therefore the material (blends) flows after melting unlike the thermoplastics, PP or PE. After reaching melting point their flow is weak. Only at a high temperature melt processing can they flow faster. Figure (4.6 B) shows the thermal stability of PHB and blend 10. At the beginning the viscosity for the blend 10 is lower than that of PHB, because it contains lubricants and plasticizers, which during processing may reduce the thermal degradation of the chains. Figure (4.6 B) shows that the viscosity for blend 10 is after one hour equal to the viscosity of PHB after 10 minutes. Blend 10 is much more stable than PHB at processing.
Figure 4.2: Various temperatures melt processing of blend 10 (A) Complex viscosity; (B) storage $G'$ and loss $G''$ modules
4.3 Results and discussions

Figure 4.3: (A) viscosity against shear rate from capillary viscometer at various temperatures for blend 10, (B) Cox-Merz rule for blend 10 at 170°C.

Figure 4.4: (A, B) Complex viscosity of PHB and blend 10 after cooling from various melt processing at temperature.
Figure 4.5: (A, B) Arrhenius plots of the viscosity for the blend 10 after cooling from various melt processing at temperature

Figure 4.6: (A) Relaxation strength versus relaxation time for blend 10, (B) Thermal stability, viscosity against the time for PHB and blend 1

4.4 Thermal degradation behavior

PHB is unstable in the melt, after reaches its melting point begins the thermal degradation [6,118]. It degrades to crotonic acid at high temperatures [6,95,96]. Melt processing at higher temperatures leads to a lower molar mass (M_w) [118,119].
4.3 Thermal degradation behavior

A lower number of nuclei for crystallization means larger spherulites. In these large spherulites, cracks were found [6,99]. If the size of the spherulites is above a critical value, then we have weaker mechanical properties. The decrease in molar mass at high screw speeds in the extruder, leads to stickiness on the metal surface and increases crystallization times. The mechanical properties were seriously affected by the processing conditions. The stress decreased with increasing processing temperatures [118]. Attempts have been made to improve the mechanical and processing properties [120,121,122,123,124]. Grassie et al. [95,96] and Kuniaka et al. [119] reported that the degradation in the temperature range from 180°C to 200°C is due to the random chain scission of the six-member ring, ester, and results in a decrease in the molar mass (M_w). The depolymerisation reaction of the esterification reaction occurs between hydroxyl and carboxyl groups. The thermal degradation of PHB and some inorganic oxides such as CaO, MgO, ZnO, PbO, PbO_2, Al_2O_3 was investigated [126]. These additives lead to the formation of many volatile products compared with PHB.

4.4.1 Experimental methods

4.4.1.1 Thermo-gravimetric analysis TG

The thermal degradation behaviour of PHB and its blends was investigated using Netzsch TG 209 thermogravimetric analysis at heating rates of 10°C min⁻¹ under nitrogen, at a flow rate of 10 ml min⁻¹. TG is followed enormous changes in the terms of time and temperature. The degradation temperature is the temperature at which the maximum of the decomposition rates is estimated.

4.4.1.2 TG-FT-IR analysis

The coupling TG-FT-IR analysis gives full information on both thermo-gravimetry and thermal degradation, respectively, using TG 209 Netzsch and FT-IR spectroscopy VECTORY from the Brucker behaviour of the sample of the blends.

4.5. Results and Discussion

4.5.1 Thermal degradation behaviour by means of thermo-gravimetry TG

The thermo gravimetric degradation curve (TG) and its derivative (DTG) of PHB and its blends curves are shown in Figure (4.8). PHB degrades at 320°C (only a large peak decomposition peak) [95]. It was observed that the blend 9 degrades at a peak temperature of 283°C (weight loss 69%), 342°C (weight loss 23.51%), and 440°C (weight loss 6.13%). PVAc degrades at 330°C and 440°C. Figure (4.9) shows DSC measurements for PHB and the blends' two main endothermic peaks; the first melting temperatures is at 175°C for PHB and
165°C in the case of blend 9. The second peak occurs at a higher temperature, and is associated with degradation at 292°C for PHB and 281°C in the case of blend 9. This result is in accordance with those of TGA and Grassie et al. [95,96].

4.5.2 Thermo gravimeter TGA and FT-IR (TG-FTIR).

TG-FTIR analysis of the blend 9 can identify the products released at different stages during the degradation process. The nature of the volatile products is important from an environmental point of view. The initial weight loss peak is shown in the figure (4.7). This due to water at 3570 cm\(^{-1}\) (283°C) and the second is due to carbon dioxide at 2350 and 670 cm\(^{-1}\) (338°C). The spectrum recorded at 283 and 291°C is in good agreement with the library spectrum for acetic acid. The small band at 3080°C cm\(^{-1}\) is related to methane. With increasing temperature, the typical bands for the acids' carbonyl group are 1760 cm\(^{-1}\) and the OH group at 3560 cm\(^{-1}\) decreases but the CO\(_2\) increases. The blends are degraded to acetic acid, carbon dioxide, water, and methane.

Figure 4.7: TG-IR spectra after degradation at various temperatures for blend 9.
4.3 Thermal degradation behavior

Figure 4.8: TG and DTG for the blend 9

TGA

Gram Schmidt

DTG

440.5 °C

-69.01 %

338.3 °C

-23.51 %

283.4 °C

-6.13 %
4.6 Conclusions to 4

1. Melt processing at higher temperatures affect PHB. This leads to a degradation process. Therefore, the rheological behaviour changes, and consequently the viscosity fall.

2. The effect of additives on PHB was governed by the processing conditions. The additives have improved rheological properties and the blends can be extruder at low temperatures melt processing (170°C-180°C) without any changing in viscosity, molar mass and crystallization behaviour (see 3).

3. The effect of the temperature of melt processing on the crystallization (see 3) and its rheological behavior may be attributed to the thermal stability of PHB and its blends. The relaxation times were calculated from oscillatory shear data with the linear viscoelastic model and the material parameters $\eta_0$, $J_g$, $J_0$ and $\lambda^\prime$. According to the results, all blends flow immediately after having reached melting point.

4. It is found that with increasing temperature melt processing the activation energy of blends increases in the opposite pure PHB.