

# PRESSURE – VOLUME – TEMPERATURE RELATIONS OF POLYPROPYLENE + POLYMER LIQUID CRYSTAL BLENDS

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## Abstract

Blends of polypropylene + polymer liquid crystal (PLC) were investigated by a pressure-volume-temperature (PVT) technique. The focus of the project was the determination of the characteristic parameters of the Hartmann equation of state, which are usable for the analytical representation of the time-temperature superposition principle. The necessary time-temperature shift factor can be calculated by the Williams-Landel-Ferry (WLF) equation. Since the WLF equation is limited in its temperature application, an equation was derived relating the time-temperature shift factor to the temperature via the reduced volume, which depends on the characteristic parameters of the Hartmann equation of state.

## Introduction

This study deals with the pressure-volume-temperature (PVT) measurements of polypropylene + polymer liquid crystal blends. PVT relations of pure PLC with varying

mesogen concentration were formerly investigated (1). Other investigations performed on this particular PLC and its blends with engineering polymers included rheology, morphology characterizations, the determination of the phase structures, and the construction of phase diagrams (2,3,4).

The focus of this project was the determination of the characteristic parameters of the Hartmann equation of state, which was performed by fitting this equation to the PVT data obtained from the Gnomix PVT apparatus. These characteristic parameters can be used for the analytical representation of the time-temperature superposition principle. The principle assures a reliable prediction of long-term mechanical properties at a given temperature over many decades of time on the basis of short-term tests. The time-temperature shift factor is calculated by the Williams-Landel-Ferry equation<sup>5</sup>. However, this equation is limited in its temperature application (6-8). Therefore, an equation was derived by Brostow et. al. (6-8) relating the time-temperature shift factor to the temperature via the reduced volume, which depends on the characteristic parameters of the Hartmann equation of state.

## Experimental

### Materials

The blend used in this study consists of polypropylene and polymer liquid crystal (PLC).

The PLC was PET/ 0.6 PHB made at Unitika Ltd., Kyoto under the trade name LC-3000. PET is poly(ethylene terephthalate) and PHB is p-hydroxybenzoic acid. The number 0.6 indicates the mole fraction of the liquid crystal (LC) constituent in the copolymer. PET/ 0.6 PHB is a thermotropic longitudinal PLC with LC sequences in the backbone along the main-chain direction, which are the reinforcing elements. This advantage and other advantages (9) of the reinforcing LC sequences confront the disadvantage of the high price of PLC's. Therefore, the PLC's are mostly used in blends with thermoplastics to lower the price but take advantage of the advantageous properties of the PLC's.

The thermoplastic matrix used was isotactic polypropylene iPP VB65 from Neste. Blends of iPP and PLC in concentrations of 5, 10, 15 and 20 wt% PLC as well as pure iPP were studied. The blends show three different orientations of the flow during injection molding. The flow orientations are either parallel, perpendicular, or non-specific to the direction of the transfer extrusion process (4,9).

### Experimental Procedure

#### Pressure-Volume-Temperature Technique PVT

The changes in specific volume as a function of pressure and temperature were determined with the Gnomix PVT Apparatus (Boulder, CO, USA) (10,11). This pressure-volume-temperature (PVT) technique offers distinct advantages over other thermoanalytical techniques because there are no baseline problems. Further, the volume is measured directly and with good sensitivity. Therefore, this technique is suitable to detect even very small changes in volume in processes such as crystallization or annealing.

In each run the sample and the confining fluid (mercury) were contained in a rigid sample cell, one end of which was closed off by a flexible metal bellow. This cell was placed into the electrically heated pressure vessel. A linear variable differential transducer (LVDT) measured the motion of the bellow end as the temperature and/or pressure changed. Volume changes of the sample were determined from the bellows deflection. This is possible since the effective cross-sectional area of the bellow and the PVT properties of the confining fluid are known. During the experiments, the apparatus measured the deviations in the specific volume of

the sample related to the initial conditions (normally 10 MPa and 20°C).

The measurements were performed in the isothermal mode at  $T_{iso} = 65, 130, 180$  and  $235^\circ\text{C}$ , e.g. for *all* components above their glass transition temperature ( $T_{g-PLC} = 61^\circ\text{C}$  and  $T_{g-PP} = -20^\circ\text{C}$ ). At each isothermal temperature the pressure was continuously raised from 10 to 200 MPa. Pressure, temperature and volume changes were recorded in steps of 10 MPa. The specific volume corresponding to  $P = 0$  MPa was extrapolated by the Tait equation using the Gnomix Software (11).

### Density Measurements

The density of the blends was measured according to the procedure of ASTM D 1505-95 (12) at  $25^\circ\text{C}$  and atmospheric pressure. After the density were measured, the samples were dried under vacuum at  $T = 50^\circ\text{C}$  for several hours.

Since our samples were buoyant in water, a special apparatus was developed. The apparatus consists of an analytical balance, a suspension jig and a glass of distilled water. The function of the jig is to submerge the sample in the water, and transfer the loading forces to the balance pan.

### Determination of the characteristic parameters of the Hartmann equation of state

The characteristic parameters  $P^*$ ,  $V^*$ , and  $T^*$  (13-17) were obtained by fitting the experimental data obtained from the Gnomix PVT apparatus to the Hartmann equation of state:

$$P^* \cdot V''^5 = T''^{3/2} - \ln V'' \quad (2)$$

The reduced volume  $V''$  is related to the specific volume  $V$  and the free volume  $V_f$  by:

$$V = V^* + V_f \quad (3)$$

$$V'' = V / V^* \quad (4)$$

where  $V^*$  is the incompressible volume and characteristic for a given material. The reduced volume  $V''$  can be calculated from the experimental volume  $V$ . The initial specific volume at atmospheric pressure and room temperature were calculated from the density values.

$P$  is the pressure and  $T$  the thermodynamic temperature, while  $P^*$  and  $T^*$  are, similar to  $V^*$ , characteristic parameters for the given material:

$$P'' = P / P^* \quad (5)$$

$$T'' = T / T^* \quad (6)$$

In this model  $T^*$  characterizes the average strength of intersegmental interactions.  $P^*$  is a complicated function of the spatial structure of the material (17-23).

## Results and Discussion

The determination of the characteristic parameters  $P^*$ ,  $V^*$  and  $T^*$  and, therefore, the fitting of the experimental data were performed using a nonlinear curve fitting procedure. The program used applies the Marquardt-Levenberg nonlinear least squares algorithm to fit the curve (24). The results are displayed in Table 1. The graphical representations of these parameters vs. the PLC concentration in the PP blends are shown in Figures 1-3.

Sample	wt% PLC	$P^*$	$V^*$	$T^*$
PLC (PET / 0.6 PHB)	100	3.58	0.601096	1553
PP w/o flow direction	0	5.37	1.000921	1589
PP+PLC w/o flow dir.	5	5.45	1.000646	1585
PP+PLC w/o flow dir.	10	5.55	1.000282	1576
PP parallel flow dir.	0	4.70	1.001008	1568
PP+PLC parallel flow dir.	5	3.69	1.001053	1546
PP+PLC parallel flow dir.	10	4.21	1.000592	1549
PP+PLC parallel flow dir.	15	4.88	1.000130	1555
PP+PLC parallel flow dir.	20	5.26	0.999689	1567
PP perpend. flow dir.	0	5.07	1.001148	1570
PP+PLC perpend. flow dir.	5	6.21	1.001324	1616
PP+PLC perpend. flow dir.	10	5.82	1.000909	1605
PP+PLC perpend. flow dir.	15	5.40	1.000443	1584
PP+PLC perpend. flow dir.	20	5.10	0.999909	1560

Table 1: Characteristic parameter of the Hartmann Equation of state for PP + PLC blends

Figure 1 discloses a significant decreasing incompressible volume with higher PLC concentrations for blends with particular and without flow direction. When the rigid PLC segments impart their orientation to the relatively soft PP matrix the blends become more squeezable.

Figures 2 and 3 reveal a nearly independence of  $T^*$  and  $P^*$  of the PLC addition and concentration as well as flow direction. Since  $T^*$  indicates the strength of the intersegmental interactions, the blends do not show strong interaction between the two components PP and PLC. In other words, the blend is nearly immiscible.

Figure 4 shows the plot of the final specific volume vs. pressure for the PP + 20 wt% PLC sample with parallel flow orientation. It reveals that with increasing temperature the volume increases because a higher temperature leads to intensified motion of the chains. This causes a larger free volume in the material. Afterwards, when the temperature was held constant and the pressure was applied the volume decreased slightly caused by squeezing out the free volume. The low isothermal compressibility is due to the efficient packing of mesogens in the PLC. As the PLC concentration increased the volume decreased. The more PLC is enclosed in the blend the more rigid LC sequences require therefore a larger free volume for their motion than the soft PP chains need.

The characteristic parameters of the Hartmann equation of state are used for analytical representation of the time-temperature superposition principle. The shift factor as well as the linear expansivity can be calculated by inserting the characteristic parameters into the equations shown below. The equation for determining the shift factor  $a_T$  is derived from the Williams-Landel-Ferry equation for the temperature dependence of the factor:

$$\ln a_T = \frac{A + B}{(V^* - 1)} = \frac{A + B}{\left(\frac{V}{V^*} - 1\right)} \quad (7)$$

where A and B are constants characteristic for a given polymer. B comes from the well-known Doolittle viscosity equation, which connects the viscosity with the free volume.

The linear expansivity is defined as follows.

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \quad (8)$$

where V is the specific volume. In conjunction with the Hartmann equation of state (2), which is in the case of atmospheric pressure as follows:

$$\ln V^* = T^{*3/2} \quad (9)$$

equation (8) results in the following expression for the linear expansivity:

$$\alpha_L = \frac{3\sqrt{T^*}}{2T^*} = \frac{3\sqrt{\frac{T}{T^*}}}{2T^*} \quad (10)$$

These equations provide better understanding of the physical significance of the characteristic parameters of the Hartmann equation of state. For example, higher values of  $T^*$  means stronger intersegmental interactions in the blend and, therefore, lower the expansivity as proven in equation

(10). The expansivity is used for miscibility prediction while the shift factor is necessary for the prediction of the long-term mechanical performance (service life) of polymers on the basis of short-term tests.

## Conclusions

The Hartmann equation of state (2) has been used to represent the PVT properties of PP + PLC (PET/ 0.6 PHB) blends. The nonlinear fitting of this equation to the experimental data was performed within an accuracy of 0.0001 %. Three characteristic parameter  $P^*$ ,  $V^*$  and  $T^*$  have been determined from 84 data points of each blend. The same equation has been previously proven as appropriate to represent our PVT data (25).

The addition of PLC to the PP caused a significant decrease of the characteristic parameter  $V^*$  with increasing PLC concentration for blends with particular and without flow direction. This is reasonable since the rigid PLC imparted its orientation to the PP matrix and the blend is therefore more squeezable.

However, the characteristic parameters  $T^*$  and  $P^*$  are almost independent of the addition of PLC as well as the flow direction during extrusion. The low values of  $T^*$  indicate a very low strength of intersegmental interactions in the blend, which reveals a nearly immiscibility of the blend components PLC (PET/ 0.6 PHB) and PP.

The determined characteristic parameters of the Hartmann equation of state can be used for analytical representation of the time-temperature superposition principle, e.g. the determination of the shift factor as well as the linear expansivity.

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Figure 1: Dependence of the characteristic parameter  $V^*$  of the Hartmann equation of state on the concentration of PET/0.6 PHB in the PP blend (blend shows different extrusion directions)

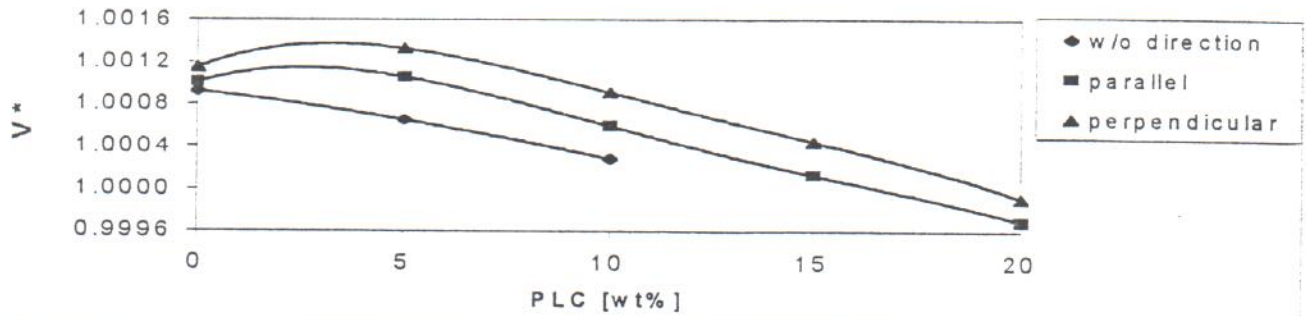


Figure 2: Dependence of the characteristic parameter  $P^*$  of the Hartmann equation of state on the concentration of PET/0.6 PHB in the PP blend (blend shows different extrusion directions)

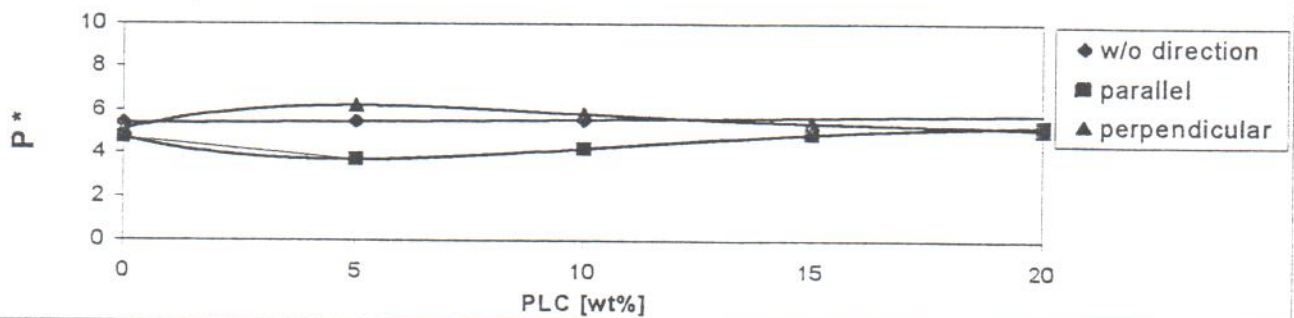


Figure 3: Dependence of the characteristic parameter  $T^*$  of the Hartmann equation of state on the concentration of PET/0.6 PHB in the PP blend (blend shows different extrusion directions)

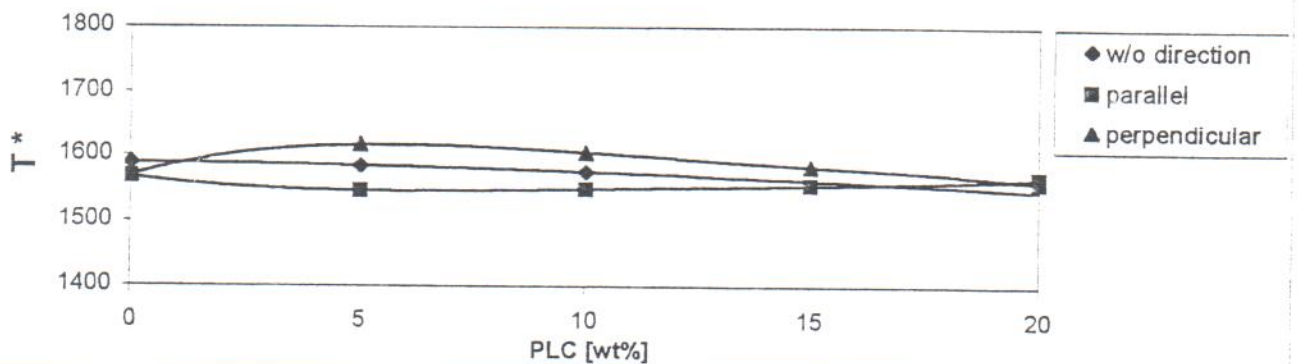


Figure 4: Pressure-dependent volume changes of PP + 20 % PLC parallel for several isothermal temperatures

