# Dow Ecolibrium™ Bio-Based Plasticizers for Flexible PVC

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## *ABSTRACT*

*PVC is widely used in a variety of wire and cable applications, usually in formulations containing petroleum based plasticizers. ). Recently, a new class of Eco-friendly plasticizers has been developed by The Dow Chemical Company. These plasticizers are derived from renewable resources (vegetable oils) and can result in as much as 40% reduction in carbon footprint compared with the incumbent plasticizers. In this study we will discuss various formulating aspects of using our seed oil based plasticizers in PVC for wire jacket type applications. DIDP will be used as the 'control' PVC plasticizer. Seed oil based plasticizers are generally not a direct plug in for the common PVC plasticizers, but it is fairly easy to substitute the 'green' plasticizer by simply using less since the new plasticizer is somewhat more efficient in plasticizing PVC when compared to DIDP.*

## INTRODUCTION

Conventional PVC formulations using petroleum derived raw materials are the industry standard for outdoor PVC sheathing. Recently renewable seed oil based PVC plasticizers have been introduced by The Dow Chemical Company for a variety of end uses.1 These plasticizers can result in as much as 40% reduction in carbon footprint compared with the incumbent phthalate plasticizers. As with any new raw material, formulating guidelines can be helpful in getting acceptable end use performance versus the performance of incumbent raw materials in a particular formulation. In this study we will compare the properties of a seed oil derived plasticizer to the properties of a conventional phthalate based PVC formulation. Standard properties like Shore A, stress/strain behavior, retention of properties after aging etc. will be evaluated and compared to the phthalate control.

## METHODOLOGY

PVC formulation details are generally proprietary and will vary with formulator's choice of raw materials etc. In this study we will use 'designed experiments', DOEs, to generate properties over a range of plasticizer, filler and PVC levels such that we can use the data to generate a model for plasticizer performance over range of compositional variables. Minimally we hope this approach will give formulators a more rapid guide to optimize their product which may incorporate the new plasticizers.

1 Dow Chemical 'Ecolibrium'® plasticizers

We will compare the performance of a DIDP based system to a seed oil based plasticizer, LPLAS® 1101 EXP1. The calcium carbonate filter had an approximate one micron particle size. The PVC used had a K value of 70. The antioxidant was CAS No. 2082-79-3. Zinc stearate we used as both the metal soap and lubricant.

**Table 1: Typical Physical Properties of Liquid DIDP, LPLAS-1101 and LPLAS-HT**

| | **DIDP** | **1101** | **HT** |
|---|---|---|---|
| **Viscosity (mPas)** | **125** | **80** | **370** |
| **Color (APHA)** | **25** | **80** | **150** |
| **Density (g/cc)** | **0.965** | **0.975** | **0.975** |
| **Water(wt.%,max)** | **0.05** | **0.1** | **0.1** |

### 'Standard' Jacket Formulation

A starting point formulation for a UV stable cable jacket2 can contain:

**Table 2: 80 Shore A Jacket Formulation**

| **Raw Material** | **phr** |
|---|---|
| PVC | 100 |
| Phthalate plasticizer | 85 |
| Lubricant | 1 |
| CaCO3 | 40 |
| Carbon Black | 6 |

### Formulations for the Model

To reduce the number of experiments needed to model formulation performance the UV blocking carbon black was not included in our initial studies. The starting point phthalate formulation ranges were:

**Table 3: Model Phthalate System Ranges (in phr)**

| | |
|---|---|
| PVC | 100 |
| DIDP | 30-85 |

2 '*Handbook of PVC Formulating*', EJ Wickson Ed., p 709, Table 27.8, J. Wiley and Sons, 1993

| | |
|---|---|
| Soap/Lubricant | 2.5 |
| Antioxidant | 0.05 |
| CaCO3 | 15-75 |

**Table 4: Model LPLAS 1101 EXP1 System Ranges (in phr)**

| | |
|---|---|
| PVC | 100 |
| LPLAS 1101 | 30-85 |
| Soap/Lubricant | 2.5 |
| Antioxidant | 0.05 |
| CaCO3 | 15-75 |

### Sample Preparation/Testing:

Samples were mixed in a 'Brabender' type bowl mixer at ~ 170$^{O}$C till homogeneous. QUV tests were done @ 60$^{O}$C, fewer than 100% RH using UV-A bulbs.

### Low Temperature Cracking

Low temperature brittleness, similar to ASTM D746, was measured for binary plasticizer/PVC blends to compare the inherent properties of our 1101 plasticizer to DOP and DIDP. The data shows 1101 is similar to or slightly better than the phthalates at the same phr level in simple binary blends of PVC and plasticizers.

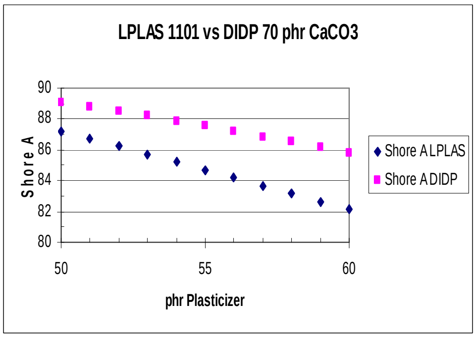
**Table 5: Low Temperature Brittleness (in $^{o}$C)**

### Formulation Results

Property data was fit to formulation variables using 'JMP'® [3] software. For model inclusion the variable needed to have a 'P' value ≤ 0.1 and preferably ≤ 0.05.

### Shore A

For a given plasticizer and filler level, LPLAS 1101 results in a lower Shore A than DIDP, and consequently when formulating for a given Shore A, less LPLAS 1101 is required when compared to DIDP. These results are shown in **Error! Reference source not found.**. A simple 'rule of thumb' suggests 10 to 20% less 1101 is needed to match the Shore A of the incumbent DIDP formulation. To replace DOP with LPLAS 1101, use about the same level of LPLAS 1101 as currently used with DOP.

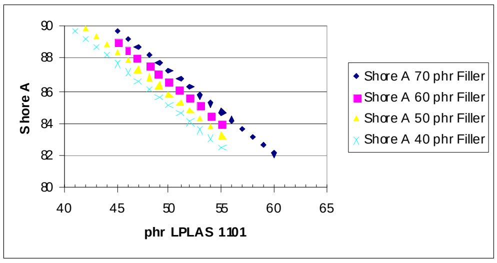



**Equation 1: Shore versus Composition**

**Shore A =**
107.6925
+-0.508333*phr LPLAS 1101
+0.070833*phr CaCO3

Figure 1: Shore A vs LPLAS and Filler quantifies the impact of filler and 1101 levels on Shore A. The response simulation for the DOE data is essentially linear in the range studied.

**Figure 1: Shore A vs LPLAS and Filler**




For LPLAS 1101 formulations using $CaCO_3$ as the filler and 100 phr of PVC Shore A can be estimated using the following equation:

| phr | DOP | DIDP | 1101 |
|---|---|---|---|
| 100 | <-40 | <-40 | <-40 |
| 50 | -20 | -30 | -35 |
| 25 | 23 | 10 | -5 |

### Formulation Results

Property data was fit to formulation variables using 'JMP'® [4] software. For model inclusion the variable needed to have a 'P' value ≤ 0.1 and

### Melt Flow Index @ 170 C 10 kg load

Although 1101 is more efficient in lowering Shore A than DIDP it can result in a higher viscosity, lower melt flow, formulation at low to moderate plasticizer levels. At higher

3 SAS Institute, V 8.0.2

4 SAS Institute, V 8.0.2

filler levels it appears have a higher melt flow, lower viscosity, than the DIDP as shown in **Error! Reference source not found.**

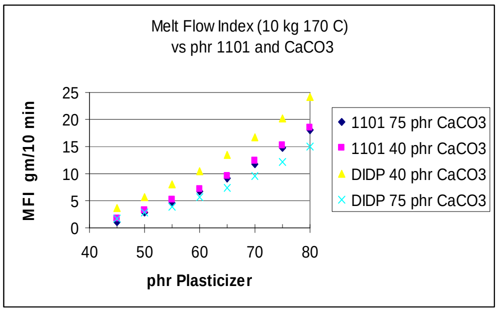



**Figure 3**

## QUV

Weatherable sheaths are typically protected from the sum with carbon black. The protection is so good it is often difficult to view performance differences for formulated systems. To visually demonstrate the differences in plasticizer UV performance we evaluated the QUV performance of formulations both unfilled and with $CaCO_3$ as the sole filler. The impact of a good UV blocker, titanium dioxide, on a filled system was evaluated as a control.

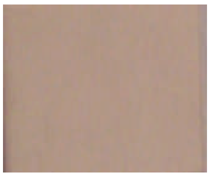
**Table 6 Compositions for QUV Study (in phr)**

| | | | |
|---|---|---|---|
| PVC | 100.00 | 100.00 | 100.00 |
| LPLAS 1101 exp 1 | 0.00 | 46.67 | 46.67 |
| ESO | 4.76 | 4.44 | 4.44 |
| DIDP | 57.14 | | |
| CaCO3 | 71.31 | 66.56 | 44.33 |
| TiO2 | | | 22.22 |
| Antioxidant | 0.12 | 0.11 | 0.11 |
| Metal Soap | 4.76 | 4.44 | 4.44 |

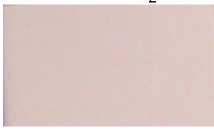
**Initial Pictures @ T = 0**

DIDP

1101

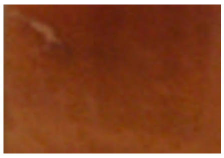


1101+$TiO_2$

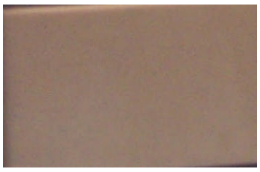


**T = 329 hrs**

DIDP



1101

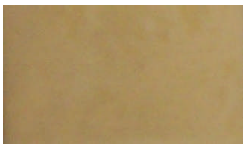


1101+$TiO_2$

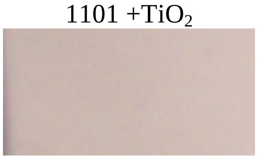
**T = 590 hrs**

DIDP

1101



1101 +$TiO_2$



**Summary**

In the present paper we highlighted the performance of a seed oil based plasticizer (LPLAS 1101) in comparison to a conventional phthalate plasticizer for PVC cable sheath applications. Seed oil based plasticizers can have a more efficient plasticizing effect than DIDP. To obtain the same hardness less plasticizer is required, which results in higher formulation melt viscosity but this should not create any problems for cable manufacturers. Non stabilized LPLAS 1101 shows good QUV performance when compared to the non stabilized phthalate. Seed oil plasticizers offer an opportunity for significant carbon footprint reduction versus petroleum based plasticizers.