5.1 INTRODUCTION

The term, compatibility with regard to the plasticizers has multidimensional parameters to a polymer technologist, compatibility means the ability of two more substances to mix with each other to form a homogeneous composition of useful plastic properties. One of the basic and essential requirements of a plasticizer is that it should be compatible with the material to be plasticized. Without compatibility a material does not meet the very definition of a plasticizer, nor it can be permanently combined with the polymer to form a useful product.

Compatibility does not only mean the ability of the substance to mix but also requires it to remain homogeneously dispersed with the polymer under almost all service conditions\(^1\). Plasticizer loss from the plasticized composition not only alters its mechanical properties, but also produces certain undesirable effects i.e. automobile fogging, and damage caused to the HIPS refrigerator linear due to loss (migration) of the plasticizer from PVC gas kit. Therefore compatibility of a plasticizer is a very important parameter and a deciding factor in the PVC compounding.

M. Wales\(^2\) studied the compatibility of plasticizers with poly (Vinyl chloride). He observed that the tendency of a plasticizer to resist
exudation from PVC under compressive stress, known technology as compatibility is treated in terms of a network model, the plasticized composition being thought of as a rubber cross-linked by crystallites. Compatibility is increased by increase solvency and decreased by increasing plasticizer molar volume. A large cross link density and/or in sufficient melting of cross-links during processing also decreases compatibility. All commercial primary plasticizers are believed to be infinitely miscible with amorphous PVC. Phase separation with occurs is syneresis and not related to any phase diagram. Swelling tests for compatibility and swelling measurements on dilute PVC gels are described.

The compatibility of suspension PVC with 12 different plasticizers was determined using calculated compatibility predictors as well as actual measurement of compatibility. Solubility parameters, were capable of classifying plasticizer of a given family in terms of their compatibility with PVC, but were not useful for comparing plasticizers from different families. The authors calculated polarity parameter, the product of the molar mass of the plasticizer and its polarity ratio which was found to be a useful predictor of activity for monomeric plasticizer.
The objective of the studies is to generate comparative data for the solvation characteristics as a measure of compatibility of the proposed plasticizer in comparison to “methyl or ethyl acetyl nicinoleate” – the reference plasticizer and the standard general purpose plasticizer DOP. Another objectives, the authors propose however, is also to determine the level to which these plasticizers can replace DOP in its compositions without showing signs of incompatibility.

5.2 SOLVATING POWER AND COMPATIBILITY

Plasticizers compatibility is a function of its solvent power. However, ideal plasticizers are only partial solvents as very good solvents will tend to produce a polymer solution rather than a useful gel structure\(^4\). Doty and Zable showed that compatibility is function of a plasticizer concentration as well as the molecular weight of the polymer. Total plasticizer level is also significant, high plasticizer concentration reduces compatibility.

The solvating power of a plasticizer depends on its molecular weight and its chemical structure. It has been observed that compounds with molecular weights of 300-500 are excellent plasticizers, higher molecular weight leading to incompatibility. Aromatic molecule due to their higher polarisability, are generally more solvating than the straight
chain aliphatic molecule. Chemical groups that enhance the solvency for PVC, are generally believed to enhance compatibility where as groups that interfere with solvency reduce compatibility. The non-cyclic ether linkages, hydroxyl and methylene groups reduce compatibility. It is also observed by a number of workers that reversal of ester grouping also affects compatibility and solvation power of the plasticizers. A change from a dibasic acid ester to a dihydric alcohol ester leads to a decrease in compatibility and efficiency⁵.

**Measurement of compatibility:**

The measurement of compatibility of the plasticizers has been a subject of interest to many investigators, through determination of their solvent power and polarity.

**Frissell**⁶ measure the effect of certain solvency groups in plasticizers structures. **Anagnostopoulos** et. al⁷ reported the development of a micro test for measurement of plasticizer/PVC compatibility. **Green hoe**⁸ used a plastisol system to define solvency as a function of different plasticizers.

**Su** and **Co workers**⁹ used GLC to determine thermodynamically the compatibility of Di-N-Octyl Phthalate (DNOP) in PVC as a function of volume concentration over the temperature range 100°C to 130°C. They
observed that at approximately 47 per hour, the heat of mixing was negative. Darby and Co worker\textsuperscript{10} reported a practical technique for predicting plasticizer compatibility through the measurement of dielectric constant and solubility parameter. The Sears and Darby Treatise\textsuperscript{11} also shows how best a three-dimensional model of butyl benzyl phthalate fits in the network of a helical model of PVC molecule.

There are a number of theoretical and practical technological tests by which likely plasticizers may be assessed for their compatibility with PVC. The studied centred around determination of $\mu$-values developed by Gee\textsuperscript{12} which indicate high miscibility with $\mu$-value of 0.55 and Hildebrand solubility parameters that are most successful when applied to polymer diluents interactions which are non-polar\textsuperscript{13-14}. Van Veerson and Meulenberg\textsuperscript{15} showed that ratio of apolar to polar carbons provides a means for calculating the effect of chemical structure of aliphatic esters on compatibility. This method is not effective, however, for aromatic, epoxy and phosphate plasticizers. Flory Huggins interaction parameters based on statistical thermodynamics agree well with the observed compatibilities\textsuperscript{16-17} but has not shown to relate with the plasticizer solvent power. Polarisability, the ability of the molecules to adapt to the surroundings, also bears a relation with solvent power and compatibility
comes forward to explain the exceptionally good compatibility of certain plasticizers greater than that expected from the compatibility predictors.

Among the practical test more significant are clear point temperature, loop compatibility, equilibrium swelling and dry blend studies. Clear point temperature also termed as solid gel transition temperature is the temperature at which mixture of PVC and plasticizer becomes clear. This gives an indication of the solvent power and compatibility both of which are greater the lower is the clear point\textsuperscript{18}, loop compatibility test\textsuperscript{19} is a simple and useful test for assessing the compatibility of plasticizers or plasticizer mixtures in a given formulation.

5.3 MIGRABILITY OF PVC PLASTICIZERS\textsuperscript{20}

The ability of the different PVC plasticizers to migrate towards a polymer in contact with flexible PVC has been investigated by A. Marcilla and Co worker. A procedure based on the monitoring of the plasticizer concentration by infrared spectroscopy has been employed. The mathematical model applied to experimental data has permitted the calculation of average diffusion coefficients and, hence, of comparison among the plasticizers (citrate, phthalates and adipates) were studied independent of the geometry of the system employed. Under the test conditions and the pro-polymer employed, phthalates seem to be the
plasticizers with the lower migration, in contrast to adipates that give the highest migration level.

5.4 PLASTICIZERS ABSORPTION

Hecker and Perry\textsuperscript{21} assumed that more compatible plasticizers would cause greater absorption and swelling of the PVC specimens immersed in the plasticizer. In the dry blend process the plasticizer is not only held on the surface of PVC particles but diffuses into the particle (adsorption). This is a kinetic process and mainly influenced by the viscosity of the plasticizer. Absorption of plasticizer into the PVC is largely influenced by the solvent characteristics of the plasticizer. Mckinney\textsuperscript{22} was the first investigator to show that resin grain actually becomes plasticized (solvated) during dry blending. At equal viscosity the plasticizers having solubility parameter closed to that of PVC will show a lower dry blend time.

1. Experimental:

Assessment compatibility of the plasticizers with PVC was made with the help of theoretical compatibility predictors like solubility parameter and specific polarisability and also by empirical methods useful in providing information on compatibility and solvent power of plasticizers. These empirical methods included determination of clear
point temperature, equilibrium swelling and dry blend time. The authors have made and effort to determine border line compatibility of some selected representative plasticizers with PVC for their sole use as well as in combination with the primary plasticizers DOP. This study was conducted, employing loop compatibility test.

2. Polarizability:

Polarizability is the measure of the ability of plasticizer molecules to get distorted in an electrical force field and therefore is the measure of its ability to adapt to its surrounding. It is calculated from the refractive index (n), molar volume (V) and Avogadros number (N) by Lorentz and Lorentz equation\textsuperscript{23}.

\[
Polarizability = \left[ \frac{n^2 - 1}{n^2 + 2} \right] \frac{3V}{4N\pi}
\]

In plasticization, it is usually more concened with comparing behaviour of plasticizers on equal volume bases, therefore it is more appropriate to measure specific polarisability of plasticizers which measures distortion in c.c./c.c. rather than to measure polarisability measuring distortion in c.c. per molecule. These values for the various plasticizers under investigation were calculated according to the equation,
Specific Polarizability = \[
\frac{n^2 - 1}{n^2 - 2} \frac{3V}{4\pi}
\]
and are reported in Table 1.

**Table 1**

Calculations of Specific Polarizability of Plasticizers.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Plasticizers</th>
<th>Refractive index (n) 25°C</th>
<th>Sp.polarizability c.c./c.c.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Di(2-ethyl hexyl) phthalate</td>
<td>1.4850</td>
<td>0.0684</td>
</tr>
<tr>
<td>2</td>
<td>Methyl acetyl ricinoleate</td>
<td>1.4560</td>
<td>0.0649</td>
</tr>
<tr>
<td>3</td>
<td>Methyl chloroacetyl ricinoleate</td>
<td>1.4667</td>
<td>0.0662</td>
</tr>
<tr>
<td>4</td>
<td>Ethyl chloroacetyl ricinoleate</td>
<td>1.4637</td>
<td>0.0658</td>
</tr>
<tr>
<td>5</td>
<td>Methyl chloroacetyl epoxy ricinoleate</td>
<td>1.4685</td>
<td>0.0664</td>
</tr>
<tr>
<td>6</td>
<td>Ethyl chloroacetyl epoxy ricinoleate</td>
<td>1.4657</td>
<td>0.0661</td>
</tr>
<tr>
<td>7</td>
<td>Methyl bromoacetyl ricinoleate</td>
<td>1.4722</td>
<td>0.0669</td>
</tr>
<tr>
<td>8</td>
<td>Ethyl bromoacetyl ricinoleate</td>
<td>1.4695</td>
<td>0.0665</td>
</tr>
<tr>
<td>9</td>
<td>Methyl bromoacetyl epoxy ricinoleate</td>
<td>1.4747</td>
<td>0.0672</td>
</tr>
<tr>
<td>10</td>
<td>Ethyl bromoacetyl epoxy ricinoleate</td>
<td>1.4719</td>
<td>0.0668</td>
</tr>
</tbody>
</table>

**Clear point temperature:**

Clear points reflect on the solvent power and compatibility of the plasticizers, both of which are higher, the lower the clear point. A low clear point indicates that the plasticizer has high gelation effectiveness.
Thus good gelling plasticizers lower the processing temperature and shorten the dry blend time which can straight way be translated into economical savings.

Veerson and Meulenberg\textsuperscript{15} categorized plasticizers according to their gelation characteristics. Plasticizers having clear point below 140°C were designated primary, between 140-170°C as secondary and above 170°C as extenders. Fast gellar too sometimes cause problems. They lead to too rapid an increase in the viscosity of the plastisole and therefore reduce their self life. In foaming application, they tend to produce higher density foams in comparison to lower solvating plasticizers\textsuperscript{24}.

The results obtained are tabulated in Table – 2. Looking at the results obtained the authors found that the present studies have resulted in the development of plasticizers with improved gelation properties in comparison to the reference, methyl acetyl ricinoleate as indicated by their lower clear point. This is clearly attributable to the solvency conferred by the polar halogen and epoxy groups. Bromo derivatives show lower gelling power (higher clear points) in comparison to their chloro counter parts probably because of their lower solvency as a consequence of lower polarity of the C–Br bond in relation to C–Cl bond. Their higher molecular weight may also cause detraction from
solvency. Based on their clear points the plasticizers can be regarded as secondary plasticizers.

**Table – 2**

**Clear point Temperature and Absorption at equilibrium swelling of PVC by various Plasticizers.**

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Plasticizers</th>
<th>Clear point temperature 0°C</th>
<th>Equilibrium swelling absorption (wt. percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Di(2-ethyl hexyl) phthalate</td>
<td>118-120</td>
<td>266.7</td>
</tr>
<tr>
<td>2</td>
<td>Methyl acetyl ricinoleate</td>
<td>160-161</td>
<td>22.8</td>
</tr>
<tr>
<td>3</td>
<td>Methyl chloroacetyl ricinoleate</td>
<td>153-154</td>
<td>29.5</td>
</tr>
<tr>
<td>4</td>
<td>Ethyl chloroacetyl ricinoleate</td>
<td>154-155</td>
<td>28.0</td>
</tr>
<tr>
<td>5</td>
<td>Methyl chloroacetyl epoxy ricinoleate</td>
<td>141-143</td>
<td>52.8</td>
</tr>
<tr>
<td>6</td>
<td>Ethyl chloroacetyl epoxy ricinoleate</td>
<td>143-145</td>
<td>54.0</td>
</tr>
<tr>
<td>7</td>
<td>Methyl bromoacetyl ricinoleate</td>
<td>156-158</td>
<td>23.5</td>
</tr>
<tr>
<td>8</td>
<td>Ethyl bromoacetyl ricinoleate</td>
<td>156-158</td>
<td>25.0</td>
</tr>
<tr>
<td>9</td>
<td>Methyl bromoacetyl epoxy ricinoleate</td>
<td>146-147</td>
<td>38.8</td>
</tr>
<tr>
<td>10</td>
<td>Ethyl bromoacetyl epoxy ricinoleate</td>
<td>148-150</td>
<td>40.1</td>
</tr>
</tbody>
</table>

In the present studies an attempt was made to determine compatibility limits for some of the representative plasticizers from among under investigation and thus to made an assessment of the improvement in compatibility achieved over the reference plasticizer methyl acetyl ricinoleate.
Although the plasticizers under investigation had shown significant increase in compatibility and solvent power in comparison to methyl acetyl ricinoleate, yet are quite far from being called primary plasticizers. Based on the result, it can be concluded that in comparison to methyl acetyl ricinoleate, halo acetylated ricinoleate can be incorporated in much higher proportion with DOP (Di (2-ethyl hexyl) phthalate) for plasticizing PVC. This is what was anticipated from the increased polarity achieved through incorporation of polar halogen groups in the plasticizers. Bromo derivatives, probably due to their lower polarity and higher molecular weight have proved somewhat inferior to their chloro-equivalence. Epoxidation has greatly help in further improving the compatibility, so that methyl chloroacetyl epoxy ricinoleate could be safely incorporated up to 50% of total plasticizer concentration.

It is noteworthy here that even the best epoxy fatty esters, so far investigated can be accommodated only up to 35% of the total plasticizers in composition. Besides higher compatibility limits the develop plasticizers will also help in economizing the processing of their PVC compositions by virtue of their lower dry-blend time and lower processing temperature.
REFERENCES


