A New Micromethod for the Determination of Plasticizer Solvent Power for Poly(vinyl Chloride)

INTRODUCTION

The interaction between poly(vinyl chloride) (PVC) and plasticizers is important in many areas of PVC processing. Considerable effort has therefore been devoted to developing practical methods for assessing the degree of interaction. These include direct measurement of solubility, dilute-solution viscosities,[1,2] and various methods based on the temperature at which PVC–plasticizer mixtures undergo an apparent phase change.[3-5] This last method has been the most widely used because of its simplicity and the fact that it can be applied to both primary and secondary plasticizers. Direct measurement of solubility is obviously restricted to plasticizers which are solvents for PVC, and dilute-solution viscosity measurements are laborious and frequently require the addition of a cosolvent (e.g., cyclohexanone[1,2] whose behavior may not be simply additive with that of the plasticizer.

We report a simple, flexible micromethod to assess the degree of PVC–plasticizer interaction based on the equilibrium swelling of individual granules of polymer suspended in plasticizer. The method can be applied to both primary and secondary plasticizers, and the results correlate well with those obtained from "apparent phase change" experiments.

EXPERIMENTAL

Materials

The poly(vinyl chloride) used in this work was Corvic D65/02 (Imperial Chemical Industries Limited, Plastics Division), chosen because of its fairly open structure and homogeneity o particle type. All plasticizers were of commercial quality and were used as received.

Method

Granules of PVC polymer dispersed in an excess of plasticizer, as shown in Figure 1, were photomicrographed (100×) at room temperature and then heated in an air-circulating oven maintained at 74°C.

The slides were examined periodically and the increase in area determined from photomicrographs using a planimeter. Heating was continued until no further expansion of the granules was detected. We found it convenient to examine the samples once a day, since expansion was generally complete within 48 hr.
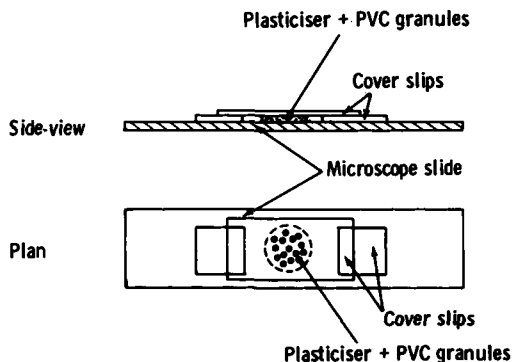

Fig. 1. Arrangement of slides used for heating PVC granules in plasticizer.

RESULTS AND DISCUSSION

The simplest method of determining the solvent power of a given plasticizer for PVC would be direct measurement of the solubility. Since this is impractical for most plasticizers, we have considered the converse system, i.e., the solubility of the plasticizer in the polymer.

It is well known that poly(vinyl chloride) in contact with a solvent swells as the latter is imbibed, and it would be possible to measure the increase in weight or size of a fabricated sample of PVC and express this as an index of plasticizer solvent power.[6,7] We have chosen to use single granules of PVC for two reasons. First, it is the equilibrium swelling which is important rather than the rate of swelling (since the latter will be greatly affected by the different diffusion rates of plasticizers[8]); hence, for rapid equilibration, the diffusion path should be as short as possible and the surface area as large as possible. Secondly, we believe that the method could be used not only to study plasticizer solvent power, but also particle morphology, in terms of the rate, and maximum value of plasticizer uptake.

The results for a series of plasticizers of widely different activities and structures are shown in Table I.

The method is least precise at extremes of swelling, since where the swelling is slight, the percentage error in measurement of the increase in area is greater, while at high swellings the contrast between the swollen granule and the background is low; and it may therefore be difficult to precisely identify the granule boundaries. Because of the latter difficulty we consider, within the limits of the experiment, that ODP and DBP are equivalent.

The order of solvent powers of the plasticizers shown is reasonable to a first approximation, with secondary plasticizers such as DOS and DOA at the bottom, DOP higher, and the plasticizers which are generally considered to be "active," such as BBP and DBP, near the top. There is, however, no absolute standard against which the results can be judged, but inspection of the table shows that the order suggested compares well with some fairly consistent literature results from apparent solution temperatures of PVC–plasticizer mixtures.

It is known that PVC has some crystalline content[12,13] and behaves, even when plasticized, as a network structure which is probably linked through the areas of crystallinity.[14-17] The system of equilibrium swelling of PVC granules might, therefore, be considered as analogous to the swelling experiments of Doty and Zable[18] who used chemically crosslinked samples. The Flory-Rehner[19,20] theory cannot, however, be applied because of the presence of fine structure in the PVC granule and the uncertain effect of plasticizers on the microcrystallites.

TABLE I
Plasticizer Solvent Power: A Comparison Between Results from
Equilibrium Swellings and Apparent Solution Temperatures

Plasticizer	Equilibrium swelling, % increase in area	Dissolving temp.,[4] °C	Critical soln. temp.,[5] °C	Gel–soln. Transition,[9-11] °C
Dibutyl phthalate (DBP)[a]	384	105	90	90–94
Octyl diphenyl phosphate (ODP)[b]	373	—	—	88–92
Butyl benzyl phthalate (BBP)[a]	72	126	96–100	104–118
Dioctyl phthalate (DOP)[c]	42	129	116–120	116–8
Dioctyl adipate (DOA)[d]	28.6	151	131–140	134–8
Dioctyl sebacate (DOS)[d]	15.0	—	—	151–2

[a] Lankro Chemicals Limited.
[b] Monsanto Chemicals Limited.
[c] BP Chemicals International Limited.
[d] Ciba-Geigy Limited.

CONCLUSIONS

The measurement of equilibrium swellings of individual PVC granules heated in an excess of plasticizer provides a simple method of assessing the solvent power of both primary and secondary plasticizers on a small scale. The relative solvent powers obtained agree well with literature results from apparent solution temperatures.

The method has two limitations. First, the time required for the swelling of the granules to reach its maximum (of the order of 48 hr); secondly, the method is less precise for either very good or very poor plasticizers.

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