The Effect of Plasticizer Solvent Power on the Aging of Poly(vinyl Chloride) Pastes

INTRODUCTION

The rheological behavior of poly(vinyl chloride) (PVC) pastes depends greatly on the plasticizer used as well as on the polymer. This is particularly true for the viscosity aging of pastes, a factor which is of great importance to the processer. In general, low-viscosity plasticizers with poor solvent action on the resin have the best aging properties.[1] Previous investigations have, however, been largely empirical (for example, refs 1 and 2); and "active" plasticizers are, by definition, those which promote rapid aging of the paste.

In connection with earlier work on suspension PVC polymers, we proposed the use of a plasticizer activity parameter α to represent numerically the solvent power of the plasticizer for PVC.[3] The purpose of the present work was to determine whether this parameter could be used to predict the aging behavior of PVC pastes.

EXPERIMENTAL

Materials. Corvic D65/02 (ICI Ltd., Plastics Division) was used to determine the plasticizer activity parameters, and the pastes were prepared using Corvic P65/54 (ICI Ltd., Plastics Division) and plasticizers of commercial quality: dioctyl adipate (DOA), Ciba-Geigy Ltd.; dioctyl sebacate (DOS), Ciba-Geigy Ltd.; dioctyl phthalate (DOP), BP Chemicals International Ltd.; Mesamoll (MM), Bayer Chemicals Ltd.; dibutyl phthalate (DBP), Lankro Chemicals Ltd.; and butyl benzyl phthalate (BBP), Lankro Chemicals Ltd.

The paste formulation used was as simple as possible, containing only polymer and plasticizer in the ratio 3:2.

Preparation of Pastes. The polymer (500 g) and plasticizer (250 g) were mixed at 60 rpm in a Hobart mixer until a paste formed. After 10 min, more plasticizer (83 g) was added and stirring continued for a further 10 min. The prepared pastes were stored at 23°C.

Measurement of Paste Viscosities. A Ferranti-Shirley cone-and-plate viscometer was used to measure the viscosity (η) of each paste at shear rates of 1–100 sec^{-1}.

Determination of Plasticizer Activity Parameters. The activity parameter α is defined as in eq. (1),[3] where χ is the Flory-Huggins interaction parameter, and MW is the molecular weight of the plasticizer:

$$\alpha = \frac{(1 - \chi)10^3}{\mathrm{MW}} \tag{1}$$

The Flory-Huggins interaction parameters were determined as described previously.[3] Briefly, the method entails measuring the apparent melting temperature (T_m) of individual granules of PVC polymer suspended in an excess of plasticizer. The χ values are then calculated from T_m using eq. (2), according to the procedure of Anagnostopoulos et al.[4]:

$$1/T_m = 0.002226 + 0.1351(1 - \chi)/V_1 \tag{2}$$

where V_1 is the molar volume of the plasticizer at T_m.

RESULTS AND DISCUSSION

Six plasticizers of widely differing activities and structures were examined in the paste aging experiments. The activity parameters are shown in Table I; the larger the value of α, the greater should be the solvent power of the plasticizer for PVC.

Typical aging curves for pastes prepared with these plasticizers are shown in Figure 1. Measurements on the paste prepared using DBP were discontinued after seven days because the viscosity of the aged paste became too high to measure on the available equipment.

TABLE I
Plasticizer Activity Parameters

Plasticizer	α
DBP	3.3
BBP	2.6
MM	2.5
DOP	2.4
DOA	1.4
DOS	0.8

It is apparent that the trend in aged viscosities correlates well with the trend of α values. The relationship is shown even more clearly in Figure 2.

There was no apparent relationship between plasticizer activity and viscosity or pseudoplastic behavior of the freshly made, or aged, pastes, as shown by Figures 3 and 4, respectively.

CONCLUSIONS

In this limited study, the aged viscosity of PVC pastes correlates well with the solvent power of the plasticizer, expressed by the activity parameter α. Hence, it should be possible to predict which plasticizers, or mixtures of plasticizers, can be used to achieve any given paste aging behavior.

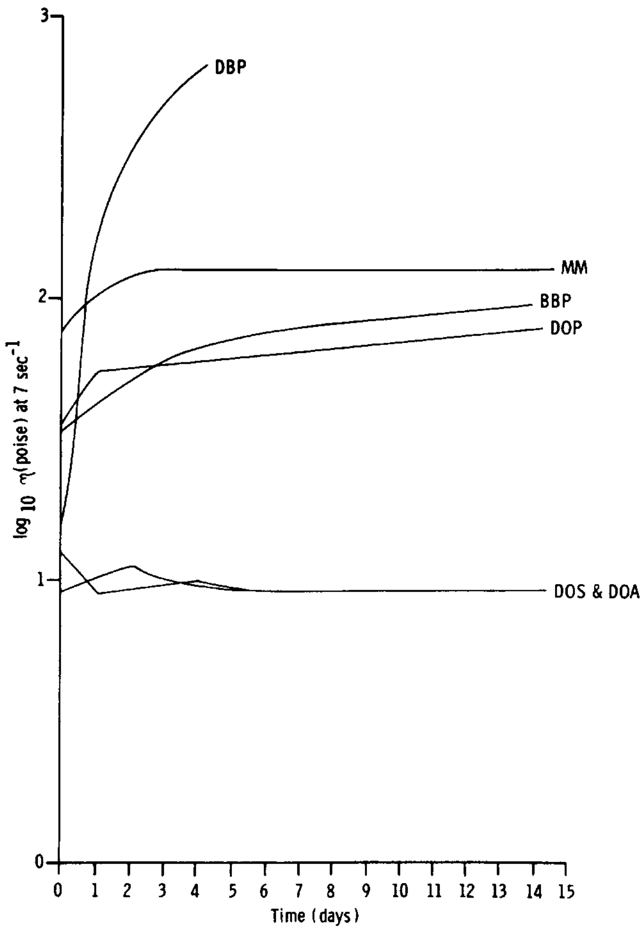

Fig. 1. Effect of plasticizers on paste aging.

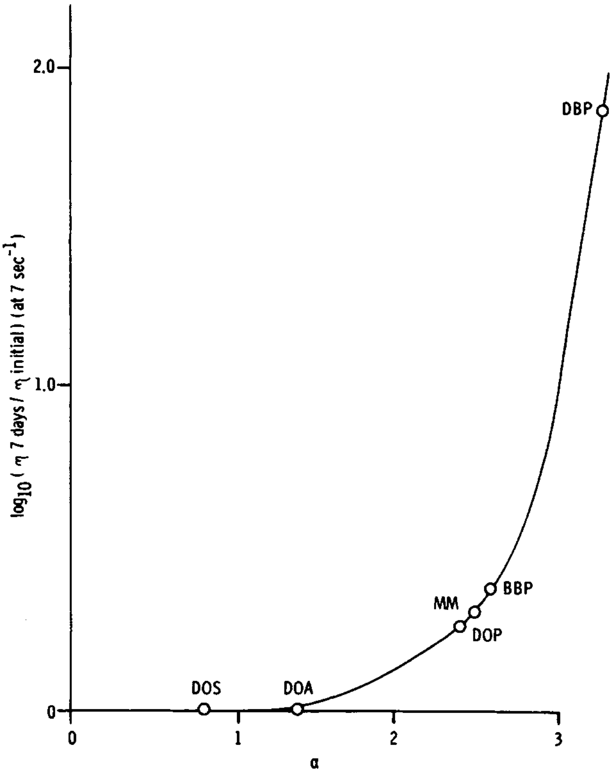

Fig. 2. Effect of plasticizer solvent power on the aging of PVC pastes.

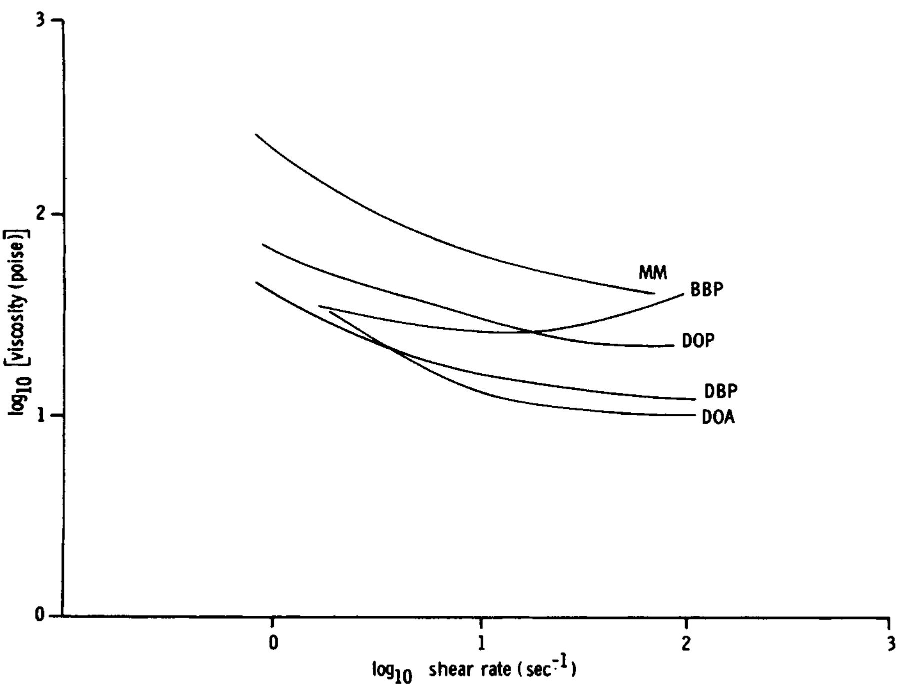

Fig. 3. Variation of viscosity with shear rate for freshly made pastes.

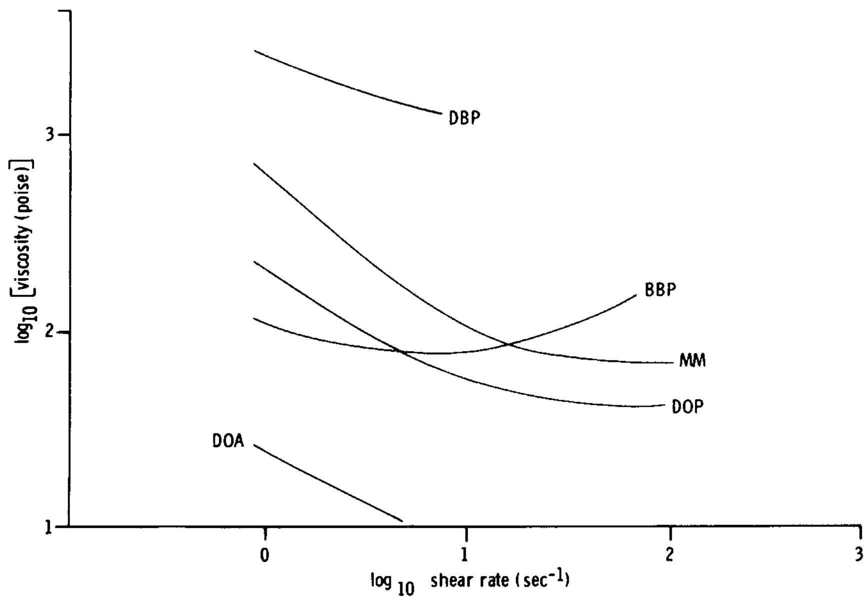

Fig. 4. Variation of viscosity with shear rate for pastes aged seven days.

The potential usefulness of these findings is greatly increased by the ready availability of α values for a large number of plasticizers from the published values of χ.[4–7]

References

1. D. S. Newton and J. A. Cronin, *Brit. Plast.*, **31**, 426 (1958).
2. G. Butlers and G. Roberts, *J. Appl. Polym. Sci.*, **15**, 2357 (1971).
3. D. C. H. Bigg, *J. Appl. Polym. Sci.*, **00**, 000 (0000).
4. C. E. Anagnostopoulos, A. Y. Coran, and H. R. Garmrath, *J. Appl. Polym. Sci.*, **4**, 181 (1960).
5. C. E. Anagnostopoulos and A. Y. Coran, *J. Polym. Sci.*, **57**, 1 (1962).
6. C. E. Anagnostopoulos, A. Y. Coran, and H. R. Gamrath, *Med. Plast.*, **43**(2), 141 (1965).
7. P. Doty and H. S. Zable, *J. Polym. Sci.*, **1**, 90 (1946).

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