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SYNTHESIS AND CHARACTERISATION OF SOME NEW PLASTICISERS

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ABSTRACT

The preparation and characterisation of new plasticisers derived from 1,3-bis(2,4,6-trihydroxymethylenephenoxide)propan-2-ol(I) as esters are described. The plasticisers were characterised by spectroscopic techniques, elemental analysis and molecular weight determination. The thermal stability and some important plasticising properties are also included, e.g. melt flow-rate. The esters included in this study are acetate, propanoate, butyrate, benzoate and oleate. The efficiency of these plasticisers was examined for PVC.

INTRODUCTION

During an earlier research programme we synthesised compound I in a one pot reaction system [1]. This product was transferred to a series of new plasticisers hoping that it would be useful for use with PVC and other polymers.

In this paper, some of the results are presented which illustrate the efficiency of these products as plasticisers for PVC. The detailed rheological properties of these plasticisers will be published later [2].

EXPERIMENTAL

Materials

Compound I was prepared in our laboratories. Polyvinylchloride (PVC), type Sicron 548 FM with K-value = 70 and commercial plasticiser dioctyl phthalate (DOP) were supplied by Iraqi Petrochemical Complex, Basrah.

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The other chemicals were used as supplied by Fluka; the solvents were purified by standard procedures.

Preparation

The esters were prepared by treating compound I with the suitable carboxylic acids in the presence of sulphuric acid as catalyst using the usual esterfication procedures [3]. The esters prepared were acetate, propanoate, butyrate, benzoate and oleate.

Characterisation

The plasticisers prepared in this study were characterised by elemental analysis and spectroscopy (infrared and NMR). These analyses were carried

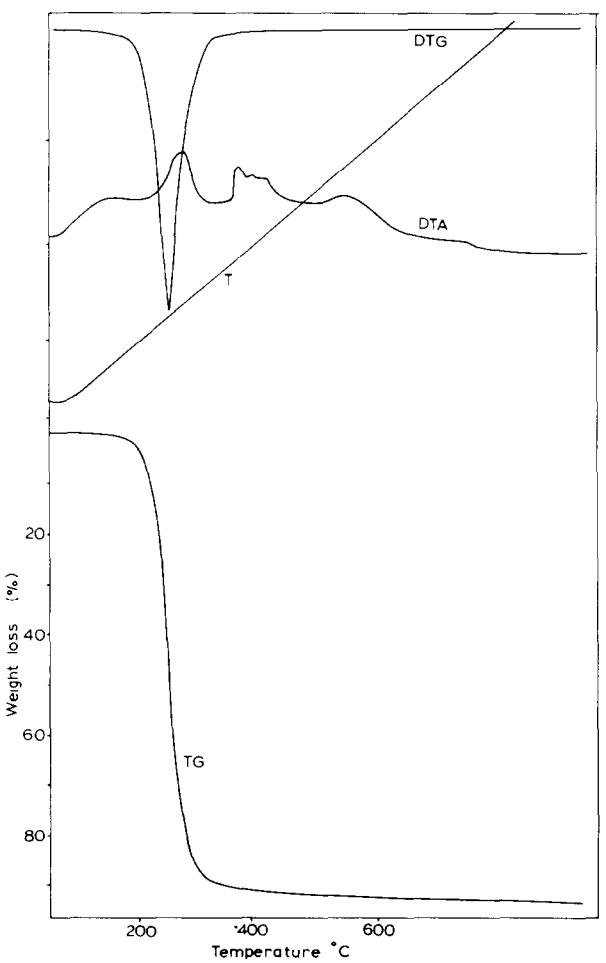


Fig. 1. Typical thermogram obtained by MOM derivatograph.

out at Alfred Bernhart Microanalytisches Laboratorium, 5251 Elbach Uber Engelskirohen, Fritz Pergl Strasse 14–16, West Germany. The molecular weights of the plasticisers were determined by applying the freezing-point depression technique in dimethylsulphoxide as a solvent, using Beckmann thermometers. The number of ester groups in the plasticisers was determined by titration [4].

Thermal analysis

The thermal stability of the plasticisers prepared in this study was studied using a MOM derivatograph. Two procedures were used: (1) isothermal analysis by heating the sample at constant temperature (140°C), following the procedure of Askar and Adam [5]; (2) heating the sample at a constant heating rate, 10° min^{-1}, and measuring the weight loss as a function of temperature. A typical thermogram is shown in Fig. 1. All the measurements were carried out against standard α-Al_2O_3 in the presence of air. The thermal stability of the plasticised PVC was also studied, the thermograms obtained are shown in Fig. 2.

Melt flow-rate

The effect of plasticisers on the melt flow-rate of PVC was examined using a Melt Index Tester Model 3/80 (Davenport Co.).

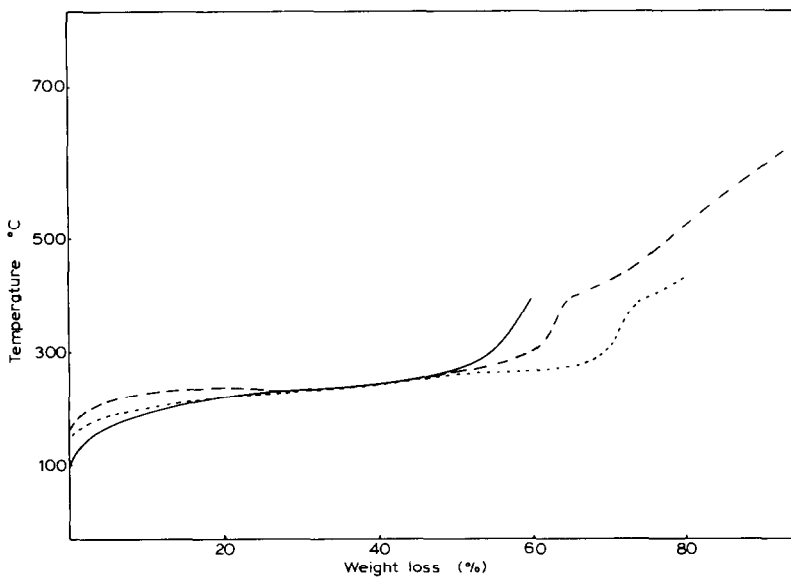


Fig. 2. The thermal stability of plasticised PVC (30%). ·····, DOP; - - - - - -, benzoate; ————, acetate.

Samples of PVC containing different ratios of plasticisers were prepared by mixing the PVC powder with the desired plasticiser solution in acetone, then the solvent was evaporated using a rotary evaporator. The homogenous plasticised samples obtained by this procedure were used for this purpose. The melt flow-rate of the plasticised samples was measured applying ASTM D1238 conditions at a temperature of 190°C under a constant load, 2.160 kg.

RESULTS AND DISCUSSION

The structure of the starting material for these new plasticisers (compound I) was confirmed in an earlier research programme [1] by the usual techniques, i.e. spectroscopic and elemental analysis. The optimal conditions for its preparation were also studied.

These new plasticisers show a good thermal stability when compared with commercial plasticisers, i.e. DOP (see Fig. 3 and Table 1. They have high boiling points and very low volatility; they also have a much greater effect than DOP on increasing the melt flow-rate of PVC (see Fig. 4). The thermograms obtained for plasticised PVC show that the thermal stability of the plasticised resin was not affected by the addition of plasticisers, thus, the decomposition temperature of the resin was almost the same.

From studying the effect of plasticisers on the melt flow-rate at different temperatures, we calculated the energy input using the general formula [6]

$$\log \mathrm{MFR} = -\frac{E}{R}\frac{1}{T} + \log k$$

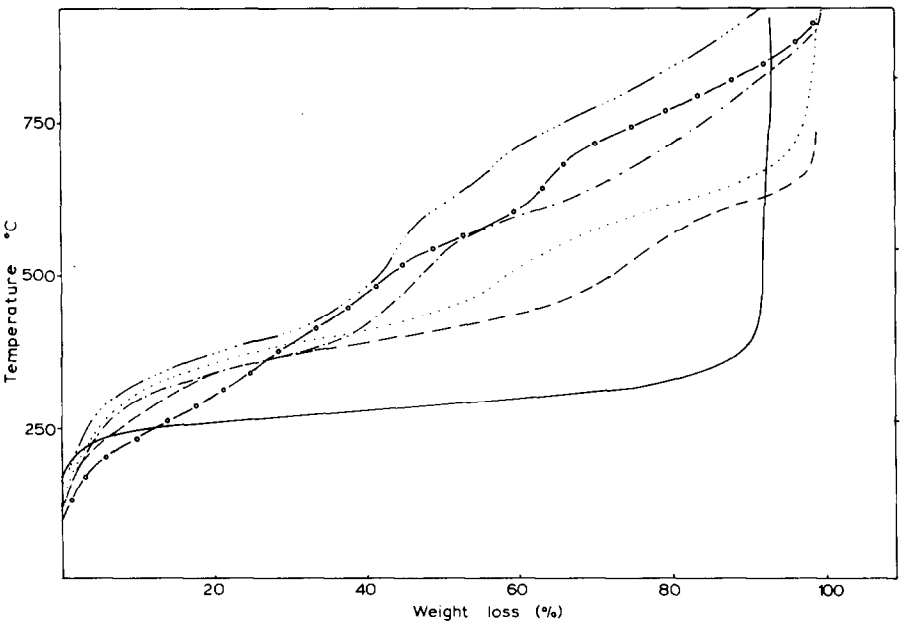
typical relationships are shown in Fig. 5. The results obtained are shown in Table 1. The energy input in the case of the new plasticisers is much lower than the energy input for the commercial plasticiser DOP.

TABLE 1

Thermal stability characteristics of the plasticisers

Plasticiser	Boiling point (°C)	Activation energy [a] (kJ mole^{-1})	Rate of decomposition (% min^{-1})	50% Decomposition temp. (°C)	Decomposition temp. from DTG (°C)
Benzoate	270	24	0.0728	295	300
Acetate	200	15	0.05319	260	230
Propionate	210	14	0.0386	320	280
Butyrate	220	21	0.0379	400	290
Oleate	285	27	0.0177	440	400
Commercial (DOP)	340	26	0.1367	220	240

[a] Activation energy for the decomposition of the plasticisers.



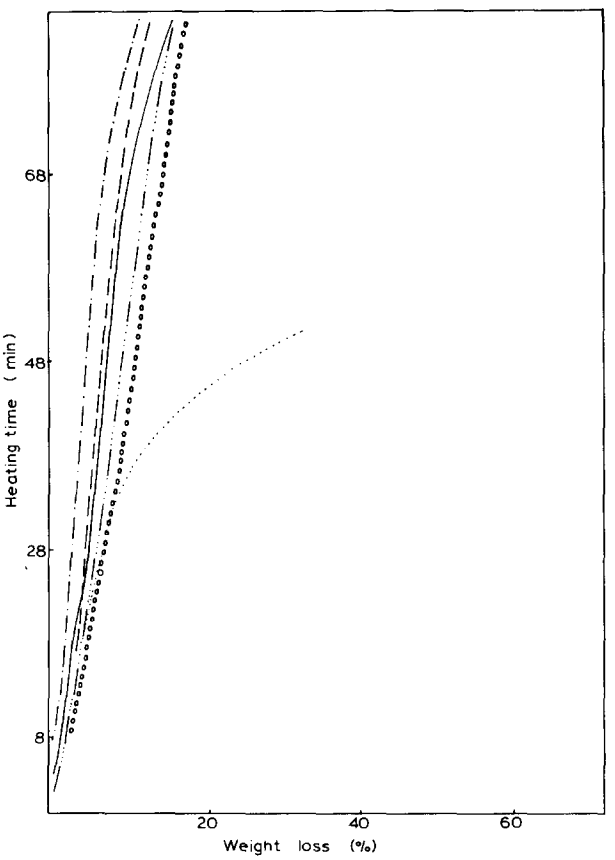


Fig. 3. Thermograms obtained for the plasticisers. (a) Weight loss as a function of temperature at constant heating rate, 10° min^{-1}. ————, DOP; ·····, acetate; —···—, propionate; – – –, benzoate; —o—, oleate; –·–·–, butyrate. (b) Isothermal curves obtained at 140°C. –·–·–, Butyrate; - - - - - -, propionate; ————, acetate; —·—·—, oleate; ·····, DOP; oooo, benzoate.

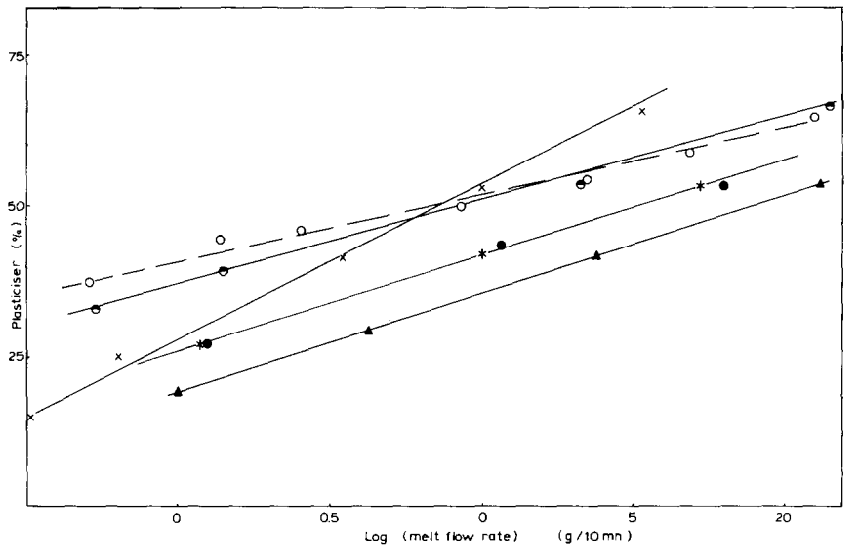


Fig. 4. The melt flow-rate of the plasticised PVC as a function of plasticiser concentration. ◒, Benzoate; *, propionate; ▲, acetate; ●, butyrate; × oleate; ⊙, DOP.

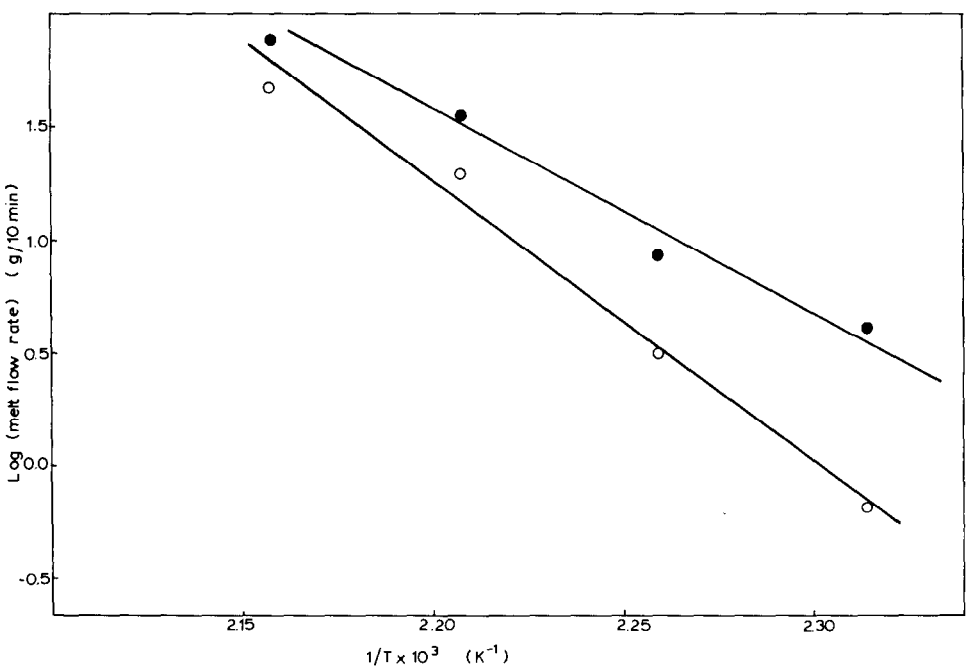


Fig. 5. The relationship between the melt flow-rate and temperature for the plasticised PVC with 50% DOP at applied loads of ●, 5160 g and ⊙, 3160 g.

The complete study of the overall properties of these plasticisers is to be published [2].

ACKNOWLEDGEMENT

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