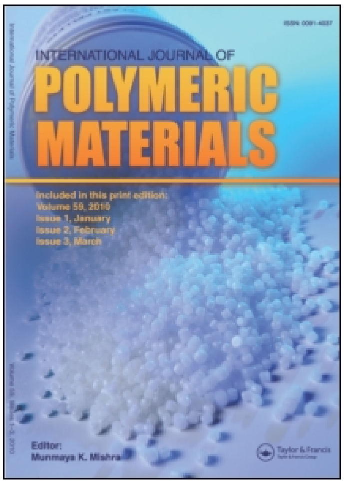

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Depression of Major Transition Temperatures of Poly(ethyleneterephthalate) Fibre by Some Model Compounds

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Depression of Major Transition Temperatures of Poly(ethylene terephthalate) Fibre by Some Model Compounds

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The effect of five flame retardant compounds on the depression of glass-transition temperature (Tg), cold crystallization temperature (Tc), and crystalline melting temperature (Tm) was examined by thermal analysis. The depression of Tg by four of the compounds was linear. The depression of Tg by the fifth compound gave a plateau-type minimum which could be due to 'super-saturation' theory or a modification of Kovacs' theory.[5]

INTRODUCTION

A study of the depression of the glass–rubber transition temperature (Tg) of polymers resulting in their plasticization, constitute a very important aspect of polymer structural studies, especially from polymer processing view point. Several workers[1–10] in this area,

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have studied different aspects of the problem using specific polymer-additive systems.

The first major series of investigations of poly(ethylene terephthalate) PET-organic solvent systems, were carried out by Sheldon and co-workers[1–4] who considered the problem from polymer swelling and crystallinity perspectives. Kovacs[5] considered the additivity of the Tgs of Polymers and diluents. Ribnick, Weigmann and Rebenfeld[6–8] examined the effect of organic solvents on the Tg of PET during the processing of PET fibre in organic solvents. Relatively more recent studies by Ingamells and others[9,10] examined PET plasticization, as manifested by segmental mobility of polymer chains and the "bimodal" nature of PET macromolecular structure in its interaction with specific functional groups in solvents. This paper examines PET plasticization based on a 'super-saturation' theory or a modification of Kovacs' additivity theory.

EXPERIMENTAL

Five model flame retardant compounds Triphenyl phosphate, TPP; Trixylyl phosphate, TXP; 1,2,5,6,9,10-Hexabromocyclododecane, HBD; Tris-(2,3-dichloropropyl) phosphate, TCP; and Tris-(2,3-dibromopropyl) phosphate, TBP were applied to poly(ethylene terephthalate), PET fibre by high temperature (140°C) 'dyeing' from their aqueous emulsions. The transition temperatures (Tg, Tc and Tm) of the treated samples and untreated controls were measured using Differential Scanning Calorimetry (DSC) at a heating rate of 10°C/min. All readings were taken on quenched samples because the enthalpy peaks of the second and subsequent runs on the DSC were better defined than the first runs.

RESULTS

Thermoanalytical data for the fibres treated with the five compounds and the untreated controls are given in tables I–V. The add-ons (%) were first obtained by weight difference of samples before and after high temperature 'dyeing.' The add-ons were then converted to volume and mole fractions.

DISCUSSION

The data from Tables I–IV when plotted show that the depression of Tg by the four compounds (TPP, TXP, TCP and TBP) was approximately a straight line as shown in Figure 1. Tables I–V show that the depression of Tc and Tm by all the compounds will give approximately a linear plot with more scatter than Figure 1. The depression of Tg by HBD is different in character, exhibiting a plateau-type minimum beyond quite a low concentration. The result show that an increase in the concentration of the additive in the polymer depresses the Tg of the polymer up to a certain point beyond which further increases in additive concentration does not lead to further depression of the Tg. This behaviour of HBD in the polymer could be due to either of these two explanations.

TABLE I

Triphenyl phosphate (TPP)

(a)

Volume fractions PET	TPP	Tg Onset Temp (°C)
1.0	0.0	75
0.989	0.014	70
0.979	0.021	68
0.959	0.041	65
0.946	0.54	55
0.918	0.082	48
0.881	0.119	48
0.829	0.171	30

(b)

Mole fractions PET	TPP	Tc Peak Temp (°C)	Tm Peak Temp (°C)
1.0	0.0	131.5	255.5
0.989	0.011	139	255
0.983	0.017	116	255
0.968	0.032	120	244.5
0.958	0.042	119	253
0.936	0.064	107	251
0.905	0.095	105	249
0.863	0.317	82.5	247

TABLE II

Trixylyl phosphate (TXP)

(a)

Volume fractions PET	TXP	Tg Onset Temp (°C)
1.0	0.0	75
0.9547	0.0451	63
0.9071	0.0929	55
0.8930	0.107	46
0.8779	0.1221	46
0.8577	0.1423	42

(b)

Mole fractions PET	TXP	Tc Peak Temp (°C)	Tm Peak Temp (°C)
1.0	0.0	131.5	255.5
0.9815	0.0185	114.5	254
0.9610	0.039	113	254
0.9542	0.0458	106	255.5
0.9475	0.0525	107.5	253
0.9378	0.0622	109	251

TABLE III

Tris (2.3-dichloro propyl) phosphate (TCP)

(a)

Volume fractions PET	TCP	Tg Onset Temp (°C)
1.0	0.0	75
0.9741	0.0259	65
0.9552	0.0448	58
0.9216	0.0784	56
0.8859	0.1141	35
0.8496	0.1504	35

(b)

Mole fractions PET	TCP	Tc Peak Temp (°C)	Tm Peak Temp (°C)
1.0	0.0	131.5	255.5
0.9867	0.0133	127	255.5
0.9768	0.0232	123	254
0.9587	0.0413	123	253
0.9388	0.0612	92.5	249.5
0.9178	0.0822	96	250

TABLE IV

Tris (2,3-dibromo propyl) phosphate (TBP)

(a)

Volume fractions		Tg Onset Temp (°C)
PET	TBP	
1.0	0.0	75
0.9986	0.0034	70
0.9937	0.0063	70
0.9926	0.0074	70
0.9908	0.0092	70
0.9812	0.0188	68
0.9615	0.0385	64
0.9347	0.0653	55
0.9256	0.0744	57
0.8993	0.1007	40

(b)

Mole fractions		Tc Peak Temp (°C)	Tg Onset (°C)
PET	TBPP		
1.0	0.0	131.5	255.5
0.9984	0.0016	126.5	255
0.9971	0.0029	137.5	256
0.9966	0.0034	133.5	256.5
0.9957	0.0043	126	256
0.9912	0.0088	122	254
0.9818	0.0182	118	254
0.9086	0.0314	112	253
0.9641	0.0359	113	253.5
0.9507	0.0493	88	249

(i) Based on some fundamental assumptions, Kovacs theory predicts the Tg in a binary polymer-plasticizer system on the following mathematical relationship

$$x\Delta\alpha_1(\mathrm{Tg}-\mathrm{Tg}_1)+(1-x)\Delta\alpha_2(\mathrm{Tg}-\mathrm{Tg}_2)=0 \tag{1}$$

where x = Volume fraction of polymer or plasticizer α_1 and α_2 are constants

Tg, Tg_1, Tg_2 are the Tgs of polymer–plasticizer mixture, plasticizer and polymer respectively.

The relationship in Eq. (1) does not depend on free volume since it is invariant at Tg, that is

$$fg_1=fg_2=fgx. \tag{2}$$

TABLE V

1,2,5,6,9,10-Hexabromocyclododecane (HBD)

(a)

Volume fractions PET	Volume fractions HBD	Tg Onset Temp (°C)
1.0	0.0	75
0.9676	0.0324	67
0.9374	0.0626	65
0.9098	0.0902	65
0.8693	0.1307	65

(b)

Mole fractions PET	Mole fractions HBD	Tc Peak Temp (°C)	Tm Peak Temp (°C)
1.0	0.0	131.5	255.5
0.9906	0.0094	128	255
0.9814	0.0186	123	254
0.9727	0.0273	113.3	253
0.9591	0.0409	118	251.5

This means that $Tg\,x$ is evaluated as a *weighted* mean of Tg_1 and Tg_2 which are dependent on the constants α_1 and α_2. There is a critical temperature Tg_c below which this relationship will no longer hold. Since if $Tg_2 > Tg_1$ then

$$Tg_c = Tg_2 - \frac{fg_2}{\Delta\alpha_2} \qquad (3)$$

Tg_x will depend only on Tg and $\Delta\alpha_1$ of the plasticizer and on fg_2. It therefore means that the lowering of Tg in such a system is not a continuous funcion of the concentration of the plasticizer. In the PET–HBD system studied, it is possible that the 'Tg' of HBD itself is so low that it is unable to produce any substantial depression of the Tg of PET beyond a certain value. This therefore, means that modifications of the theory of Kovacs[5] could explain this result. It is however, not possible to prove this suggestion since the Tg of HBD could not be measured because the compound could not be quenched to a glass.

(ii) The method of incorporation of the additive is such that the temperature at which it is incorporated is substantially higher than

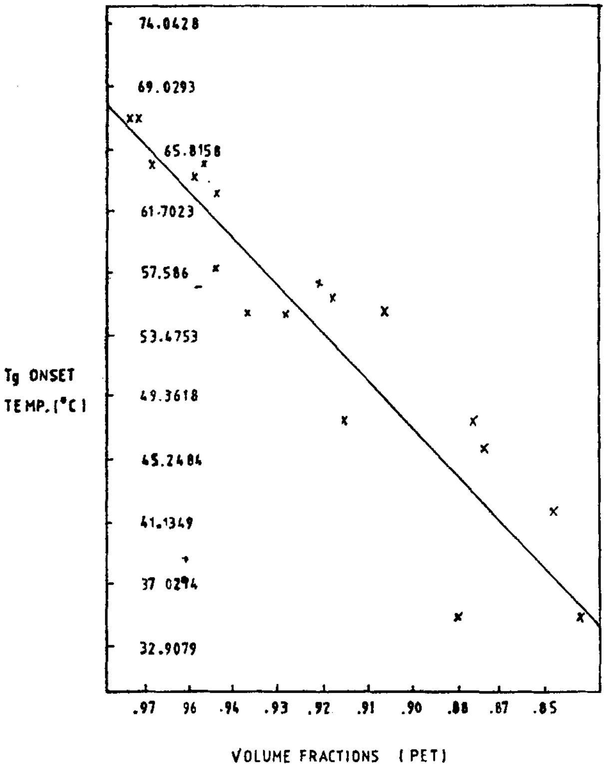

FIGURE 1 Tg Onset temperature as a function of volume fractions (PET/HBD).

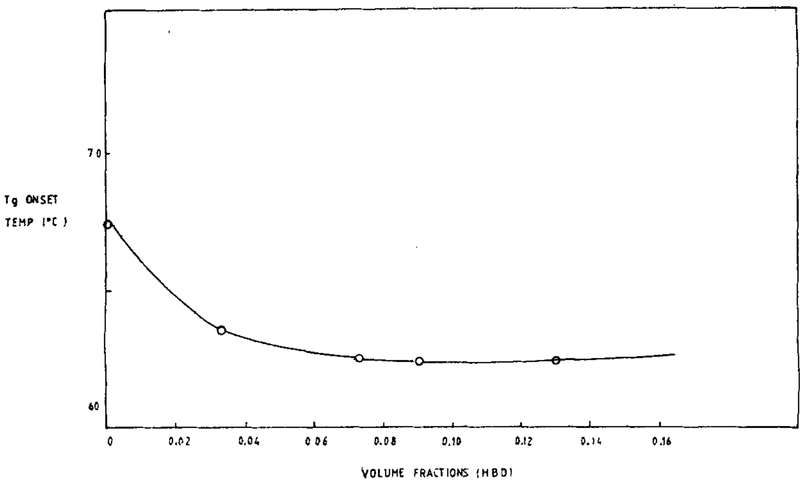

FIGURE 2 Tg Onset temperature as a function of volume fractions (PET/HBD).

the Tg of the polyester fibre. If the additive is more soluble at the high temperature, it is possible that on levelling, the additive is present in a 'super-saturated' state. In that case the excess of additive over the saturation solubility will no longer be truly dissolved and will cease to have a lowering effect on the measured Tg.

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