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Melting-reactive dyes for mass coloration of synthetic fibres—part I: perylene-3,4,9,10-tetracarboxylic acid dianhydride in poly(ethyleneterephthalate)

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Abstract

Mass coloration of poly(ethyleneterephthalate) (PET) by using a melt-reacting dye is described, and affords an economical favorable and environmentally friendly method of coloration. Perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTAD) was used as a melting-reactive dye in poly(ethyleneterephthalate) and showed high thermal stability. A chain-extending reaction was confirmed by UV–vis and IR spectroscopic analysis. The effect of the proportion of the added PTAD on the intrinsic viscosity of the polymer was studied, and increasing amounts resulted in increased intrinsic viscosity. The higher viscosity is beneficial to the spinning process. The light fastness of the colored fibres was as high as 7. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive dye; Mass coloration; PET; Perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTAD); Chain-extending; Light fastness

1. Introduction

As synthetic fibres (polyester, nylon, etc.) typically have a compact structure and high crystallinity, the choices of dyes and dyeing methods for them has long attracted researching interest. Since the first reactive dyes were marketed by ICI in 1956 as the Procion M dyes, followed by the Procion H and Cibacron (CIBA) as well as Remazol (HOE CHST) dyes in 1957, reactive dyes represented by far the most important development in the field of synthetic dyes. Reactive dyes were characterized by a fibre-reactive component bonded to an appropriate azo, anthraquinone, phthalocyanine or metal complex dye [1–3]. Our further investigations were focused on finding a new reactive system, and resulting in a range of new dyes.

Reactive blending offers attractive opportunities for developing new materials with useful combinations of properties [4]. Thus, new covalent bonds are generated in situ during melt blending. Therefore, this method could also be applied on the mass coloration of synthetic fibres containing reactive terminal groups. In this paper, perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTAD), which contains two carboxylic anhydride moieties, is shown to be a useful melt-reactive dye. Esterification takes place during blending PTAD and poly(ethylenetereph thalate) (PET) in the melt phase. Such a method is useful in that it does not use a traditional aqueous dyebath, thus avoiding pollution problems.

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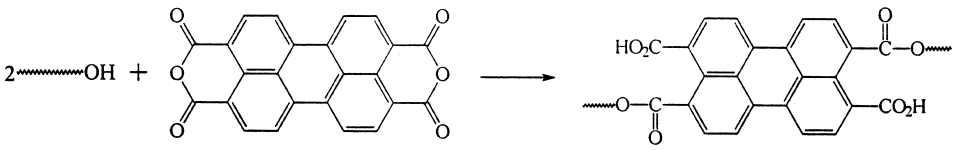

2. Experimental

2.1. Materials

The reagents were commercially available and used without further purification.

2.2. Instruments

UV–vis spectra were measured on a Lambda 20/2.0 spectrophotometer. IR spectra were run as KBr pellets on a Pargon 1000 FT–IR spectrophotometer. The thermal stability of samples were evaluated using TGA-7 thermal analyser (Perkin Elmer) at a heating rate of 20°C/min in a nitrogen atmosphere. The intrinsic viscosity was measured in a 60/40 (wt.%) mixture of phenol and tetrachloroethane.

2.3. Procedures

PET with an intrisic viscosity of 0.6 was prepared by a typical polycondensation method from bis(β-hydroxyl terephthalate). Granulated PET and PTAD were mixed carefully and then dried in an oven at 130°C, to a moisture content of less than 0.01% by weight. Mass coloration was carried out in a Haake Rheocord 90 batch mixer equipped with roller blades. The mixing temperature, mixing speed and mixing time were maintained at 280°C, 100 rpm and 6 min, respectively. The mixture (PET–PTAD) was then extruded, cooled and pelletized. The resulting product was extracted with acetone in a Soxhlet extractor, and dried in air. Colored PET fibre was formed under laboratory conditions by means of an Instron 4467 capillary rheometer. It was extruded from the melt with a temperature of 273°C into air with a temperature of 20°C. After passing through the atmospheric medium, the colored fibre was collected at a speed of 100 m/min. For testing light fastness, the sample and the standard were mounted on a frame partly covered with an opaque sheet, leaving the other half exposed in the outdoors for 15 days. The faded sample was compared with the standard [5].

3. Results and discussion

3.1. Spectroscopic analysis

The λ_{max} of PTAD and PET–PTAD were 523 and 520 nm, respectively, which indicated a little bathochromic effect (Fig. 1). The reaction of PTAD with terminal groups in PET was confirmed by the IR analysis, that is, the absorption peak of 1769 cm^{-1} (cyclic anhydride group) disappeared and the peak of 1717 cm^{-1} (ester group in PET) was broadened by the newly formed ester and carboxyl groups from the chain-extending reaction (Fig. 2).

3.2. Effect of added amount of PTAD on intrinsic viscosity of PET

As a result of a chain-extending reaction, the molecular weight and intrinsic viscosity of the PET–PTAD composite is increased relative to PET itself. This is beneficial to the spinning process of colored PET. Usually, addition of a chain-extender in an amount equivalent to the number of terminal hydroxy groups in the polyester will result in the highest molecular weight and intrinsic viscosity [6]. However, the equilibrium nature of esteritication might cause derivation from this ruler. From the Mark–Houwink relationship and the equation for the esterification equilibrium, the increase of intrinsic viscosity as $\Delta(\ln \eta)$ is given by:

$$\Delta(\ln \eta) = \ln \eta - \ln \eta_0 = \ln \frac{\eta}{\eta_0} = \alpha \ln \frac{K_e}{\sqrt{K_e^2(a-1)^2 + 2K_e a + 2K_e + 1} - 1} \quad (1)$$

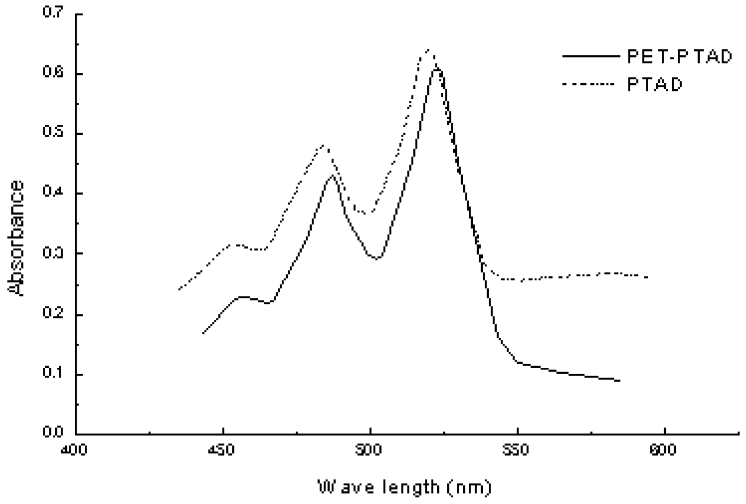

Fig. 1. UV–vis spectra of PTAD and PET–PTAD.

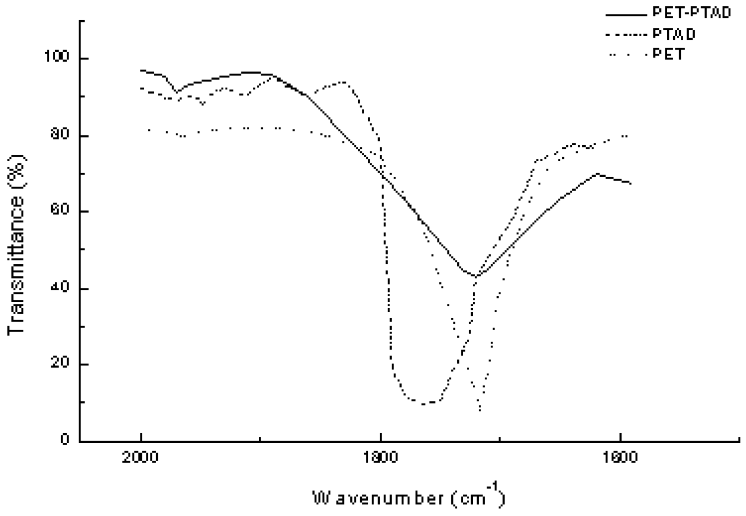

Fig. 2. IR spectra of PET, PTAD and PET–PTAD.

where α is a constant in the Mark–Houwink relationship; K_e is the empirical esterification equilibrium constant; a is the ratio of added PTAD to the number of initial hydroxyl terminal groups.

$$\frac{d[\Delta(\ln \eta)]}{da} = 0, \qquad a = 1 - \frac{1}{K_e} \tag{2}$$

Therefore,

$$\Delta(\ln \eta)_{max} = \alpha \ln \frac{K_e}{2\sqrt{K_e - 1}} \tag{3}$$

Eq. (2) indicated that the value of a, which led to the highest intrinsic viscosity, depended on the value of K_e, and is less than 1. The value of a would approach to 1 when K_e is large (i.e. as in an irreversible reaction).

As seen from the experimental results (Fig. 3), the maximum value of $\Delta(\ln \eta)$ was obtained when a reached 0.83. Also, the value of K_e (esterification

equilibrium constant) was calculated to be 7.69 from Eq. (2).

3.3. Thermal analysis

In principle, dyes and pigments for mass coloration of synthetic fibres require high thermal stability in melt extruding and spinning. PTAD, PET and the reactive extrudate (PET–PTAD) were subjected to the thermal analysis. The TG curves in Fig. 4 indicate that PTAD degraded at higher temperature than PET and PET–PTAD, for the same heating rate. Thus, PTAD is more than adequately thermally stable for this application.

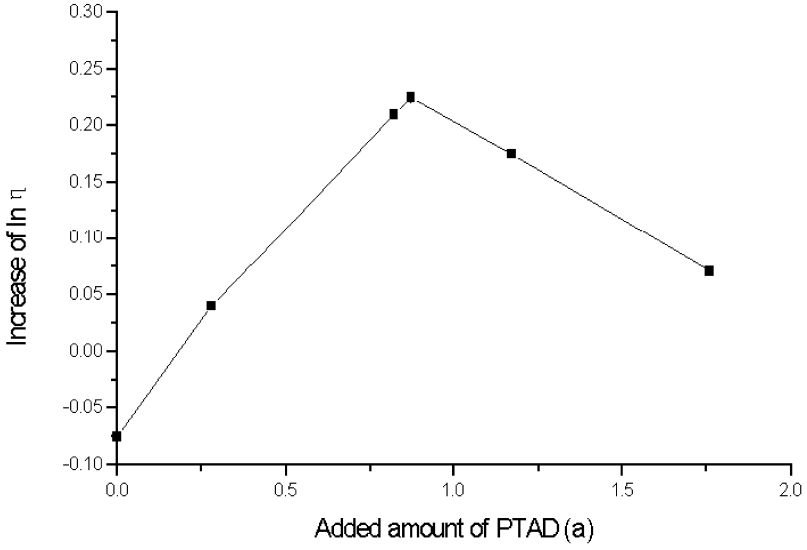

Fig. 3. Effect of added amount of PTAD on the intrinsic viscosity of PET.

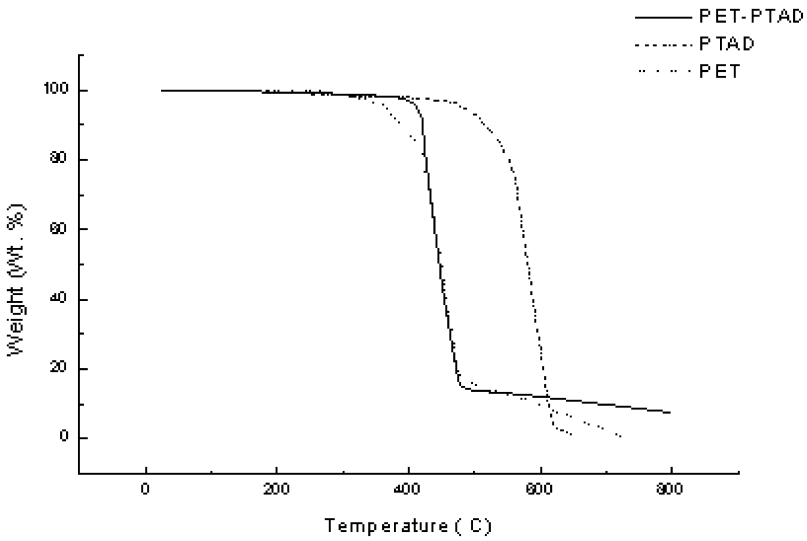

Fig. 4. Thermal analysis of PET, PTAD and PET–PTAD.

3.4. Light fastness

Light fastness is one of the most important properties of textile fibres. The light fastness of the PET–PTAD colored fibre was found to be as high as 7. This is probably due to the presence of highly conjugated aromatic rings in the polymeric chain, which act as a screen against UV radiation [7].

4. Conclusions

On the basis of the experimental results, reactive mass coloration provides an economically favorable and environmentally friendly method of coloration. The reactive dye used in this method showed high thermal stability and resulted in the increased intrinsic viscosity of PET by a chain-extending reaction. The colored fibre thus obtained had good light fastness.

Acknowledgements

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