LUMINESCENCE AND DEGRADATION OF NYLON POLYMERS II: QUENCHING OF FLUORESCENT AND PHOSPHORESCENT SPECIES

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Summary

The effect of various photostabilisers on the fluorescent and phosphorescent species in nylon-6,6 polymer has been studied and related to their known light-stabilising activity in the polymer. Alkali metal halides quench the fluorescent species in the polymer in the order I > Br > Cl > F and this follows the same order as their light stabilising activity. Alkali and transition metal salicylates quench the phosphorescent species in the polymer and are effective photostabilisers, while phenyl salicylate, which is a poor stabiliser, exhibits weak quenching and salicylic acid itself, which is a non-stabiliser, exhibits no quenching. The sensitising action of the anatase form of titanium dioxide pigment, added as a fibre delustrant, is normally counteracted by coating the pigment particles with a manganese compound. The effect of this treatment is to quench the phosphorescence emissions from the pigment and the polymer.

Introduction

In earlier studies [1 - 4] (see ref. 4 for Part I) we reported on the nature of the luminescent species in commercial nylon-6,6 polymer and discussed their role in sunlight-induced oxidation. In particular we found that the excitation wavelengths required to produce maximum fluorescence and phosphorescence emissions were 360 and 290 nm respectively. This indicated that the emissions were from different impurity species.

To achieve a satisfactory solution to the problem of nylon photo-oxidation a wide variety of "stabiliser compositions" have been developed [5 - 8]. Of these, the compositions based on either the alkali metal halides or various organometallic compounds appear to be the most frequently used [9 - 17]. Interestingly, however, there is little information in the literature regarding their mode of operation. Here we report on the emission properties of polymers containing typical examples from the two classes of stabiliser. This

paper only deals with significant changes that occur in the emission properties of the polymer.

A second problem encountered with the nylon polymers, which is possibly more commercially important, is that of the photosensitising effect of the delustrant added to improve the appearance of the polymer in fibre form [5, 8, 18, 19]. Here the anatase form of titanium dioxide is the pigment most widely used and over the years it has been found that manganese-containing coatings on the surface of the pigment particles have proved to be the most effect photostabilisers [5, 8, 12 - 16]. In the final part of the paper, therefore, we have again tried to assess the effect of these coatings on the photoactive luminescent species.

Experimental

Materials

Nylon-6,6 film (200 μm thickness) containing no commercial additives was supplied by I.C.I. (Plastics Division) Ltd. Nylon-6,6 polymer samples in fine "chip" form containing anatase and rutile pigments (about 0.5%) were supplied by I.C.I. (Fibres) Ltd. Anatase and rutile pigments were supplied by Tioxide International Ltd.

Sodium iodide, sodium bromide, sodium chloride and sodium fluoride were of Analar quality. Salicylic acid, phenyl and various alkali and transition metal salicylates were supplied by Graesser Salicylates Ltd. (N. Wales, Gt. Britain).

The salicylates were incorporated into nylon-6,6 film by immersing the film into solutions of the salicylates (about 1.0%) in an isopropanol–water mixture (50/50 vol.%) for about 2 h.

Luminescence measurements

Corrected fluorescence and phosphorescence spectra and phosphorescence lifetimes were obtained using a Hitachi Perkin–Elmer MPF-4 spectrofluorimeter as described earlier [4].

Results and discussion

Effect of halide ions

The addition of alkali metal halides improves the photostability of the polymer in the order I > Br > Cl > F [9]. Here we have carried out two separate types of experiment to assess possible quenching action by the halide ions. In earlier work [4] we showed that oxidised nylon-6,6 salt contained the same type of fluorescent species as the commercial polymer itself. It was thus possible to examine firstly the quenching effect of halide ions on these species in aqueous salt solutions and secondly the corresponding qualitative effect when the fluorescent species are in a polymer matrix.
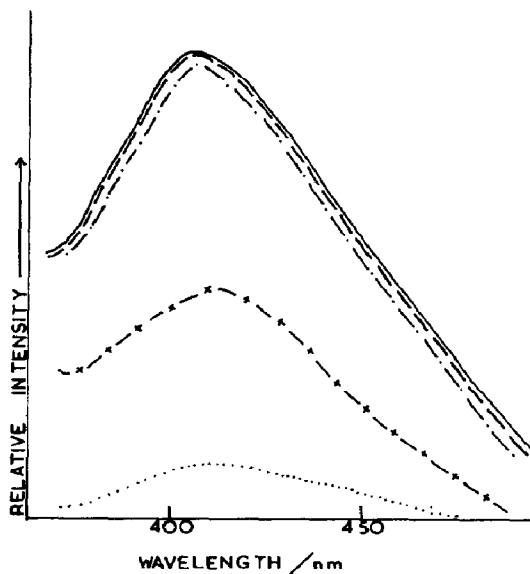
Fig. 1. Fluorescence emission spectrum of nylon-6,6 film (excitation λ_{max} = 360 nm) before (———) and after 2 h immersion in a molar solution of sodium fluoride (– – –), sodium chloride (–·–·–), sodium bromide (–×–×) and sodium iodide (......).

The first type of experiment was described in a preliminary communication [20] where it was found that linear Stern–Volmer plots were obtained with the fluorescent impurities in aqueous solution. The halide ion deactivation efficiency showed the same trend as that of the protective action of the halides in the polymer. In the second type of experiment samples of nylon-6,6 polymer in film form were immersed under standardised conditions for 2 h in 1 M aqueous solutions of the sodium halides. Figure 1 shows that a similar trend of halide quenching activity is observed.

Effect of salicylates

In this section of the work the effects of various metal salicylates on the intensity and lifetime of the phosphorescence emission from nylon-6,6 film were examined. The effect of salicylates on the fluorescence emission from the polymer could not be examined owing to overlap by the strong fluorescence from the salicylates themselves. Again, these compounds were chosen for study because they are reported to be effective nylon photo-stabilisers [7, 8, 17]. For comparison purposes phenyl salicylate, which is a poor stabiliser, and salicylic acid, which is a non-stabiliser [21, 22], were also examined. The results are shown in Table 1.

To compensate for any screening effect due to direct absorption by the salicylates their concentrations were adjusted so that at 290 nm (the excitation wavelength maximum of the nylon phosphorescent impurities) their optical densities were about 0.5. It is seen that all the alkali and transition metal salicylates examined effectively reduce the intensity and lifetime of the phosphorescence emission. However, when the central metal atom is

TABLE 1

Effect of salicylates on nylon-6,6 phosphorescence (excitation λ_{max} = 290 nm)

Additive	Phosphorescence emission intensity 410 nm (relative)	Phosphorescence emission lifetimes τ (s)
Nylon-6,6 control	1.0	2.20
Salicylic acid	1.0	2.20
Phenyl salicylate	0.75	1.20
Sodium salicylate	<0.10	<0.10
Magnesium salicylate	<0.10	<0.10
Aluminium salicylate	<0.10	<0.10
Manganese salicylate	<0.10	<0.10
Copper salicylate	<0.10	<0.10
Chromium salicylate	<0.10	<0.10

replaced with a phenyl ring the quenching effect is not so marked. The acid gives no significant quenching. Again these experiments establish a correlation between quenching efficiency and photostabilising activity, in this case involving the photoactive phosphorescent α,β-unsaturated carbonyl impurities [1 - 4]. The importance of the presence of the metal atom in the stabiliser for its phosphorescence quenching action may well be related to a similar result obtained for the nickel(II) ketoxime chelates in polypropylene. There it was found that the nickel and the oxime ligand had to be reacted together for phosphorescence quenching and photostabilisation to occur [23].

Effect of TiO$_2$/manganese combinations

Figure 2 compares the low temperature emission spectra of the anatase and rutile forms of titanium dioxide. It is seen that on a relative basis anatase has a much stronger emission (λ_{max} = 540 nm) than rutile which emits weakly in the infrared (λ_{max} = 820 nm). The excitation wavelength maxima of the two modifications are 340 and 370 nm respectively. These correspond to the absorption maxima of the pigments when dispersed in thin polymer films.

As noted above, although anatase is the more photoactive pigment it is nevertheless preferred as a delustrant. In order to reduce the photoactivity of anatase to commercially acceptable levels the surfaces of the pigment particles are coated with a manganese compound (usually manganese phosphate) or various manganese-containing compositions. When typical manganese phosphate coated particles were examined under the same excitation conditions as in Fig. 2 no luminescence was observed. Thus the presence of the manganese coating markedly affects the emission properties of the pigments. When the coated pigment was added to the polymer again no emission at 540 nm was observed. Indeed, if the pigment loading in the polymer was greater than about 0.5% then even the native phosphorescence
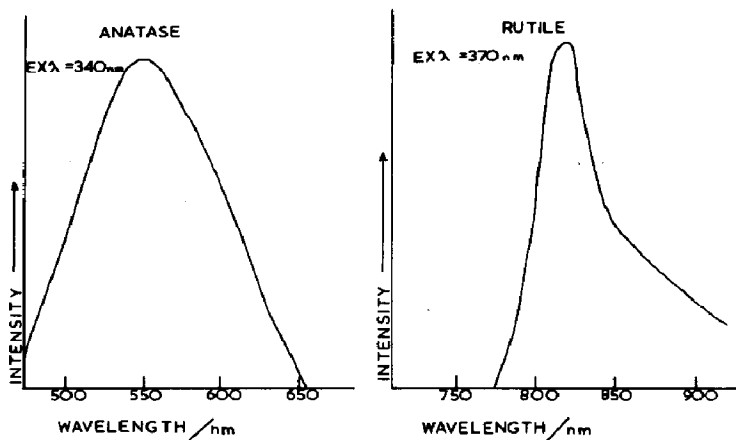
Fig. 2. Low temperature (77 K) emission spectra of (a) anatase (sample sensitivity × 30, bandwidth 4 nm) and (b) rutile (sample sensitivity × 100 max, bandwidth 20 nm).
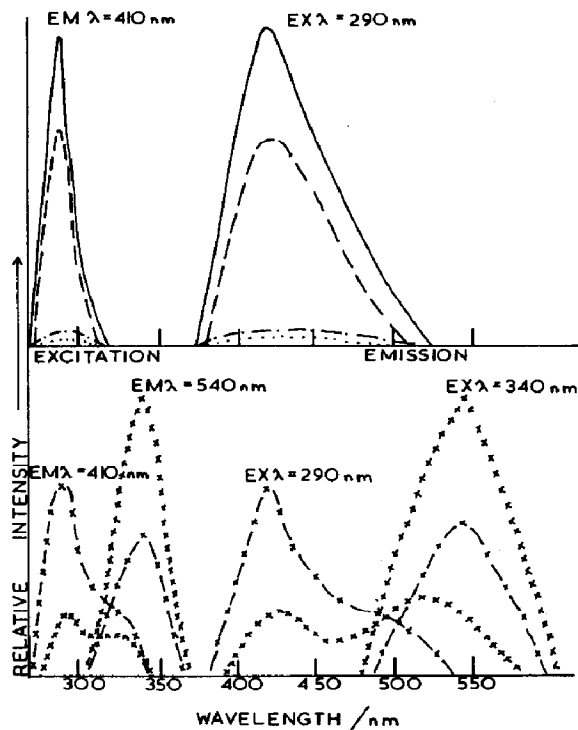

Fig. 3. Phosphorescence excitation and emission spectra of nylon-6,6 containing no TiO_2 (——), 0.5% rutile and 0.5% rutile + 25 ppm Mn^{2+} ions (– – –), 0.5% anatase and 0.5% anatase + 25 ppm Mn^{2+} ions (–×–), 2% anatase (××××), 0.5% Mn^{2+} coated anatase (–·–·) and 2% Mn^{2+} coated anatase (.....).

due to processing impurities [4] was significantly reduced (Fig. 3). When, however, a manganese compound was added to the polymer, but not as a surface coating on the pigment, no significant effect on the emission from either the pigment or the polymer was observed (Fig. 3).

Thus the presence of manganese ions on the surface of the anatase particles appears to give two quite distinct quenching effects. First the phosphorescence emission of the pigment is quenched. Second at the pigment loadings used in commercial practice the photoactive phosphorescent impurities are also quenched. Thus it is clear that there are at least two quenching processes that can occur in the delustred polymer and that on a mechanistic basis the relative importance of the two is probably determined by the type of delustred fibre used [5].

Acknowledgments

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