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The *Cis–trans* Isomerization and Lightfastness of Azo Dyes Dispersed in Thermoplastic Fibers with Different Structural Features

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ABSTRACT

The cis–trans *isomerization of* 4-N,N-*diethylaminoazobenzene dispersed in two polyamidic fibers has been studied. The fibers were obtained by blending polyamide 6 with appropriate amounts of an aromatic copolyamide, which allowed a controlled enhancement of the* T_g *value of the polyamide. The different fastness properties of the dyed materials could be explained in terms of the observed different structural features of the blends. © 1997 Elsevier Science Ltd*

Keywords: *cis–trans* isomerization, 4-diethylaminoazobenzene, blended polyamide 6 fibers, structural features, fastness.

INTRODUCTION

Polyester fibers are a typical example of a semicrystalline polymer in the glassy state at room temperature. However, their glass transition temperature ($T_g = 77°C$) is lower than that usually employed during the dyeing process. Dyeing is thus carried out on the polymer in the rubbery state and the dye enters the free volume of the hot fibers. On cooling, this volume reduces, entrapping the dye and progressively hindering its molecular motions, as confirmed by the decrease of its *cis–trans* isomerization rate, this phenomenon being also associated to aging [1]. As a consequence, the dye is protected to a significant xtent from the degrading effect of light, wet-washing, and dry-cleaning.

When severe thermal treatments are carried out on polyester fibers reaching an extended crystallization ($>50\%$), the free volume model of the polymer changes to the pore model, and the dye inside the pores becomes more susceptible to the attack of light and washing water. This happens, for instance, in the case of transfer printed textiles where a stringent thermofixing procedure is carried out to equalize fabrics from fibers of different thermal histories. The induced change from the free volume model to the pore model structure is irreversible [2, 3]. Highly crystalline polymers such as polypropylene, which have a pore model structure and no chemical affinity for dyeing agents, cannot be dyed by direct processes. However, recent studies on the characterization of polymer blends obtained from parent compounds miscible in the melt, suggest that a direct dyeing process, as well as good fastness properties can be achieved promoting a free volume structure, as in the case of a suitably blended propylene. The other possible way that could be considered for carrying out the dyeing of pore model structured fibers, namely dye transfer printing, is not feasible, as the very limited extent of the amorphous phase of crystalline substrates cannot adequately fix the dye. This is the case with highly ordered cellulosic fibers, such as cotton, which exhibit a pore model in their supermolecular structure; they cannot be dyed by sublimation methods. On the other hand, these natural polymers, being capable of chemical and physical interactions with the dye, can be dyed by direct processes.

In humid polyamide 6 (PA6) fibers, the semicrystalline polymer is in the rubbery state, its T_g being lower than room temperature. Under these conditions, the molecular mobility is rather high and this results in a limited lightfastness of the dyed material, and in a fast *cis–trans* thermal return of an irradiated azo dye inside it. On the other side, when polyamide fibers are thoroughly dried, their T_g value increases to a temperature as high as 50°C and their behavior resembles that of polyester. However, the chemical nature of polyamide fibers offers the advantage of a higher affinity for azo disperse dyes, which leads to a markedly greater lightfastness. As noted above, the plastifying effect of water on the dyed PA6 greatly influences the fastness of the dye, in particular when the material undergoes washing with hot water (60–90°C). As this undesired phenomenon is directly correlated to the low T_g value of humid polyamide, an enhancement of this value should led to an increased fastness of the dyed fiber. On this basis, in this present work a controlled enhancement of the T_g value of the polyamide fiber has been obtained by blending PA6 with appropriate amounts of an aromatic copolyamide (PA6T/6I) ($T_g = 130°C$), polymers having been previously found to be miscible in the melt [4]. The resulting materials have been characterized and the kinetics of the *cis–trans* isomerization of an azo dye, 4-*N*,*N*-diethylaminoazobenzene, dispersed in them has been studied according to reported procedures [5]. The observed different structural features of the blends can explain the different fastness of the dyed materials. Some results of this work have been recently reported [6].

EXPERIMENTAL

The polymers used in this work were a general purpose nylon 6 (F34 GRILON) (PA6) and an amorphous copolyamide (GRIVORY 21) (PA6T-6I), supplied by EMS Chemie (CH). Blends of PA6 and PA6T-6I with weight ratios of 90/10 and 70/30 were prepared by melt mixing in a Gimac single screw extruder. The screw speed was adjusted to 30 rpm and the die temperature was 240°C.

Differential scanning calorimetry (DSC)

The thermal behavior of the blends was studied using a differential scanning calorimeter (Perkin Elmer DSC-4) operating at the following conditions: the specimens (*ca* 7 mg), encapsulated in aluminum pans, were rapidly heated from 50 to 220°C at a heating rate of 40°C min^{-1}. All the measurements were performed under a constant flow of dry nitrogen. An indium standard sample was employed to determine the thermal lag due to the scanning rate.

Dynamic mechanical thermal analysis (DMTA)

Measurement were carried out with a dynamic mechanical thermal analizer (Polymer Laboratories, Ltd) MK III with the sample presented in the tensile mode at a frequency of 1 Hz and a strain ×1. Polymer specimens in the form of small injection moulded bars ($20 \times 5 \times 0.5$ mm^3) were investigated in the temperature range from −20° to 120°C with a heating rate of 3°C/min.

Cis–trans isomerization kinetic measurements

The polymer films were dyed with 4-*N*,*N*-diethylaminoazobenzene as will be described in Section 2.4. Film dye concentration was chosen to obtain an absorbance value in the range 0.6–1.4 at the desidered wavelength. For the isomerization measurements, each film was sandwiched between two quartz plates and exposed for 15 min in a thermostated compartment to the light of a 100-W tungsten lamp, a time long enough to reach a photostationary state. Under this treatment the configuration of the dye changed from the original more stable *trans* form to the *cis* form. After irradiation, the film was quickly introduced into the cell compartment of a Beckman DU 640 spectrophotometer thermostated at the same temperature of the irradiation. The *cis–trans* thermal return was monitored as the change in absorbance at 421–423 nm, i.e. at about the absorption maximum of the *trans* isomer. As reported in previous studies [5], while in the rubbery state of the polymer such a reaction usually follows a simple first order kinetics, below the T_g value it is characterized by a multiplicity of simultaneous first-order processes. Thus, linear trends of $-\ln(A_\infty - A_t)$ vs time do not occur in the glassy state, A_∞ and A_t being the absorbance values at 'infinity' time and at a given time t, respectively. The extent of *cis–trans* isomerization was expressed by the equation

$$y = (\mathrm{A}_t - \mathrm{A}_0)/\mathrm{A}_\infty - \mathrm{A}_0$$

where A_0 refers to 'zero time'.

Dyeing procedure

An AHIBA apparatus was used for the dyeing experiments. The films were first washed at 60°C in a water containing 0.25% (by weight) of tenside, then washed with water and dried. Dyeing was carried out in water (bath ratio 1:40) with 0.08% (by weight) of 4-*N*,*N*-diethylaminoazobenzene, starting at 40°C, then raising the temperature to 98°C and maintaining at this temperature for 1 h.

Light and wet-washing fastnesses

The determinations of light fastness were performed using a Xenotest Hanau 150 S (Heraeus); assessments were carried out according to UNI 7639 (ISO 105-B02). Wet-washing fastness tests were carried out according to UNI 7638 (ISO 105-C01/03/04).

RESULTS AND DISCUSSION

The increase of the T_g value of the blends when compared with that of plain PA6 is evidenced in Fig. 1, that reports the absorption data vs time relative to the *cis–trans* isomerization of the 4-*N*,*N*-diethylaminoazobenzene coloring the polymeric matrix in the dried pure polymer at 21° and 50°C, and in the dried 70/30 PA6/PA6T-6I blend at 50°C. In the former case, on going to the higher temperature, the trend of $-\ln(A_\infty - A_t)$ vs time becomes quite linear, thus revealing that a simple first order kinetic equation governs the process, thus suggesting the occurrence of the rubbery state. Such a linearity is clearly absent in the case of the blend, which appears to be still in the glassy state.

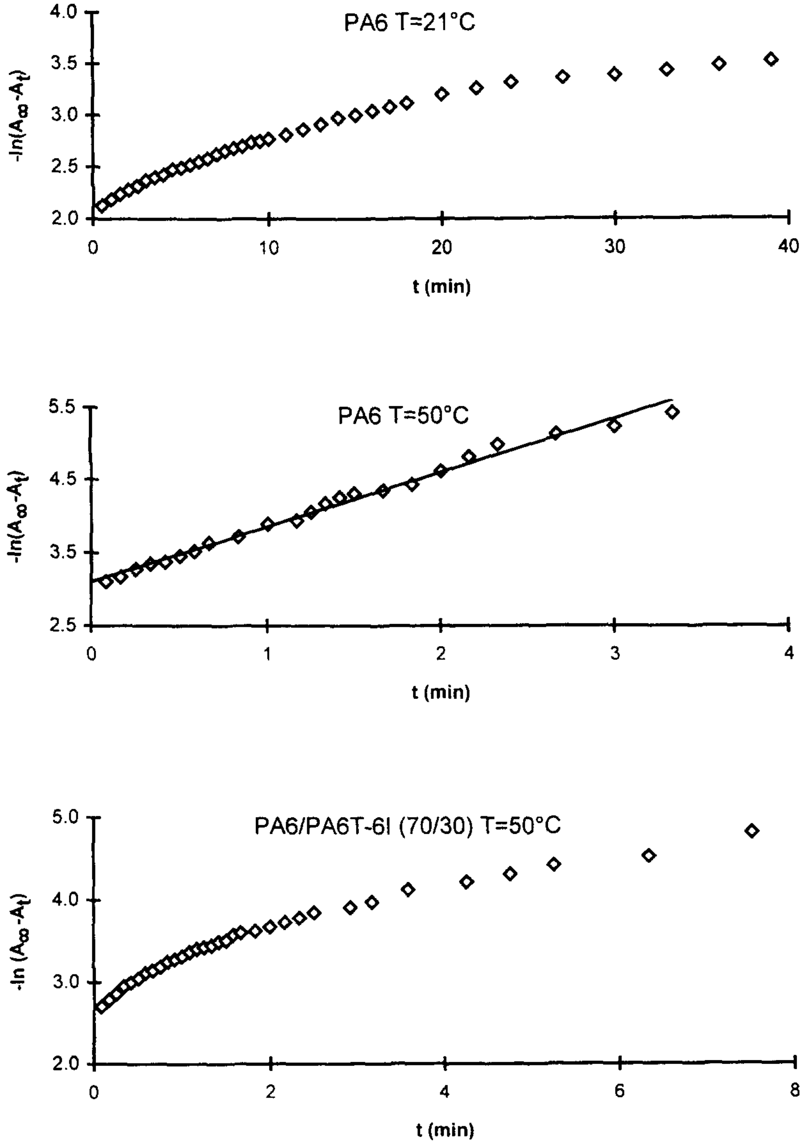

Fig. 1. *Cis–trans* isomerization of 4-*N*,*N*-diethylaminoazobenzene in different polymeric matrices followed by spectrophotometric measurements.

The above observations are in accord with the results of our previous studies [5] according to which, below the T_g value, the kinetics of the *cis–trans* thermal return of an irradiated azo dye in a polymer matrix could be resolved only by considering the process as a multiplicity of independent parallel first order reactions, instead of a simple first order reaction as occurs above the T_g value.

The curved trends of $-\ln(A_\infty - A_t)$ vs time observed in the present case have been rationalized by assuming the occurrence of two parallel reactions with relative importances rather close to each other. The optimization procedure gave values of the Arrhenius parameters in the range 24–30 for the $\ln A$ term (A in s^{-1}) and in the range 18–22 kcal/mol for the E_a term. Examples of k values (s^{-1}) at 21°C are:

$$k_1 = 2.62 \times 10^{-3},\ k_2 = 2.64 \times 10^{-4}\ \text{(PA6)};\ k_1 = 1.84 \times 10^{-3},$$
$$k_2 = 7.07 \times 10^{-5}\ \text{(70/30 PA6/PA6T-6I)}.$$

Interpreting the kinetic data in the framework of a two-reactions model has lowered the standard error of estimate (ϵ) to values as low as 0.01–0.03, while the corresponding values obtained in the case of a simple reaction model were around 0.08. On the other hand, values of ϵ lower than 0.03 have been obtained, as expected, when a simple first order process was assumed for the isomerization at the highest temperature, this fact having been considered as evidence of the attainment of the rubbery state.

Besides the enhancement of the T_g value, blending PA6 with PA6T-6I has been found to lower significantly the overall process rate. This is shown in Fig. 2, which reports a comparison between the reaction extent

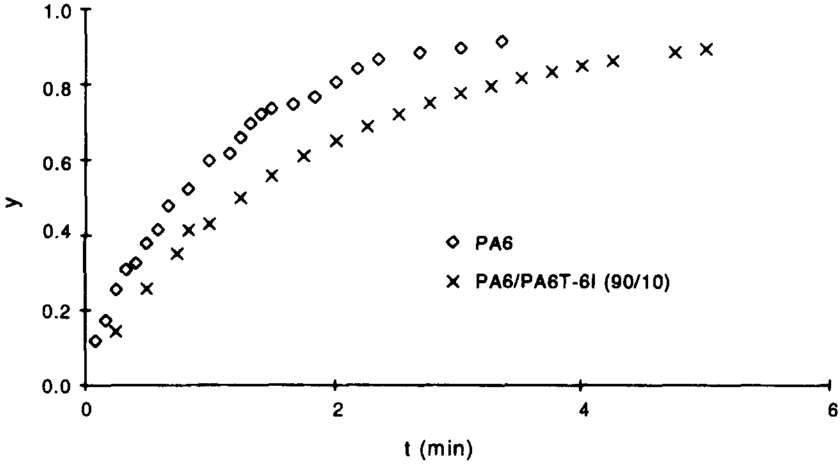

Fig. 2. Time courses of *cis–trans* isomerization of 4-*N*,*N*-diethylaminoazobenzene in plain and blended PA6 at 50°C.

vs time in plain PA6 and that in 90/10 PA6/PA6T-6I at 50°C, chosen as examples.

As noted above, an enhanced T_g value leads to an increased fastness of the dyed fiber. This effect is also shown by the decrease of the isomerization rate. The slowness of the process evidences the occurrence of a highly entrapped dye, which results in a higher protection against external agents as light and washing water.

The enhancement of the T_g value induced by blending has been confirmed and quantified by DSC measurements. The data in Table 1 refer to polymeric materials at different levels of dryness.

TABLE 1

T_g Values (°C) Obtained by DSC Measurements, of Polyamidic Materials Containing Different Amounts of Water (a, b, and c)

Fiber	*PA6*	*PA6/PA6T-6I (90/10)*	*PA6/PA6T-6I (70/30)*
a	41	67	82
b	30	42	54
c	−6	n.d.	43

a: Thoroughly dried materials (105°C for 45 min).b: Dyed materials employed in the *cis–trans* isomerization study (left 9 d in desiccator at r.t.).c: Humid materials.

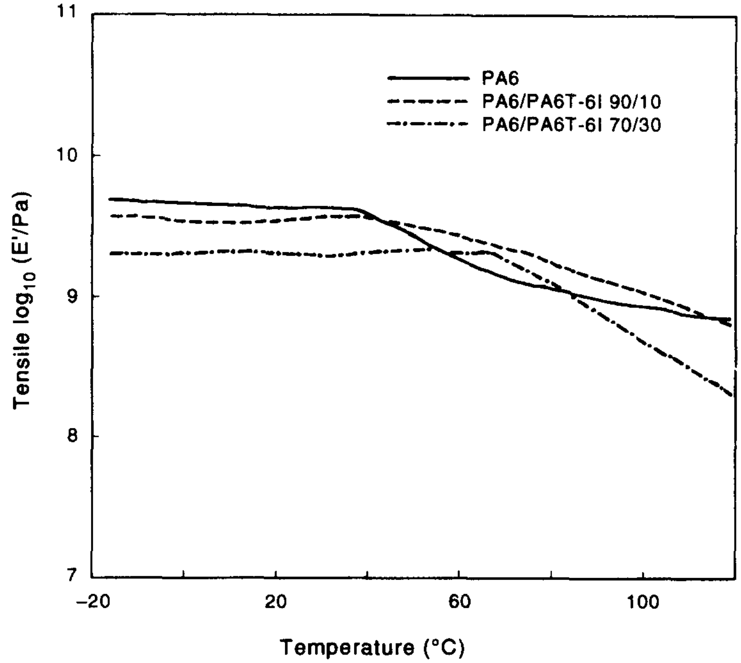

Fig. 3. DMTA measurements of plain and blended PA6.

TABLE 2
Light and Wet-washing Fastnesses of PA6 and PA6/PA6T-6I Films Dyed with 4-*N*,*N*-diethylaminoazobenzene

Fiber	*PA6*	*PA6/PA6T-6I (90/10)*	*PA6/PA6T-6I (70/30)*
Light	3	5	3/4[a]
Wet-washing (40°C)	4/5	5	5
Wet-washing (60°C)	2	4/5	4/5
Wet-washing (90°C)	1	4/5	4/5

[a] This value is influenced by photochromic effects.

DTMA measurements also support the increase of the T_g value with blending. Typical curves of log E' vs temperature are reported in Fig. 3 for plain and blended PA6: they show that the storage modulus drop occurs at higher temperatures on going to higher content of aromatic polyamide. Such moduli are lower for blended than for plain PA6 up to about 40°C, but above this temperature the trend can reverse.

The light and the wet-washing fastnesses of PA6 and PA6/PA6T-6I films are reported in Table 2. In both cases, a significant improvement in the material properties is obtained with both the blends. In particular, the 90/10 PA6-PA6T-6I blend appears to be the more resistant one. The results in Table 2 are essentially in accord with the conclusions made above on the basis of the kinetic behavior of the irradiated azo dye in the different polymeric matrices under investigation.

CONCLUSION

A controlled enhancement of the T_g value of polyamide 6 was obtained by blending it with suitable amounts of an aromatic copolyamide. This was evidenced by a kinetic study carried out on the *cis–trans* isomerization of 4-*N*,*N*-diethylaminoazobenzene dispersed in the blend. In fact, the kinetics of the isomerization of the considered azo dye reflects the structural features of the dispersing polymeric matrix. The enhancement of T_g was also confirmed by DSC and DMTA measurements. The structural modifications induced by blending led to a significant increase of the fastness of the dyed polyamidic fibers.

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