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THERMOGRAVIMETRIC ANALYSIS OF BLENDS BASED ON NYLON 6 AND A THERMOTROPIC LIQUID CRYSTAL COPOLYESTER

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In memoriam of Professor J. G. Fatou

Abstract

The thermal stabilities of blends between Nylon 6 and the liquid crystal copolyester Vectra A were investigated by thermogravimetric analysis under dynamic and isothermal conditions. The theoretical mass loss curves were compared with the experimental ones in order to establish the influence of blending on the thermal stabilities of the pure polymers. The characteristic degradation temperatures and the relative values of the volatilized matter percentages were obtained from the dynamic curves, and the effect of the blend composition was analysed. The resulting data, together with the analysis of the activation energies, demonstrated that blending has an important effect on the thermal stability of Vectra A, which undergoes a considerable destabilization in the presence of Nylon 6.

Keywords: blends, Nylon 6, thermogravimetry, Vectra A

Introduction

In recent years, many polymer blends have been developed as an alternative to the synthesis of new materials [1]. The properties of polymers can be improved in a desired way and with low economic cost by means of blending. In particular, the blending of liquid crystal polymers (LCPs) with thermoplastic polymeric matrices has become of considerable technological interest for a number of reasons [2]. LCPs are known to exhibit anisotropic order together with a low melt viscosity and a low coefficient of thermal expansion [3]. The blending of LCPs with conventional polymers can lead to low-cost products with liquid crystal behaviour and better processability properties. During processing of the blend, the LCP phase can adopt a fibrillar structure, thereby producing an in situ composite reinforcement which results in improved mechanical behaviour.

An understanding of the thermal stability of these materials is essential in order to determine their potential applications. Blending can influence the thermal stability considerably, in a manner which can not be predicted merely from the

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behaviour of the corresponding homopolymers [4]. However, not many studies have been made of the degradation behaviour of polymer blends in the literature [5–13] and, to the best of our knowledge, very few thermogravimetric studies of blends containing thermoplastic and LCPs have been published [14, 15].

Several authors have pointed out that interactions can occur between the polymer components and their degradation products and this can lead to significant changes in the thermal stabilities of the blends [5–7, 13]. As this kind of interaction involves the diffusion of small species between phases, the degree of dispersion of the phases can have an important effect. The influence of miscibility and that of chemical interactions between the components on the thermal stabilities of the corresponding blends have also been considered [10–12].

In this work, we report an analysis of the thermal stabilities of blends formed between Nylon 6 and the liquid crystal copolyester Vectra A, based on *p*-hydroxybenzoic acid and 2-hydroxy-6-naphtoic acid. The thermogravimetric analysis was carried out under dynamic and isothermal conditions in order to analyse the effects of blending on the thermal stabilities of the individual polymers.

Experimental

The thermotropic liquid crystal copolyester used in this study was the commercial product Vectra A 950 from Hoechst SA, a wholly aromatic copolyester consisting of 27 mol% of 2-hydroxy-6-naphthoic acid (HNA) and 73 mol% of p-hydroxybenzoic acid (HBA). Nylon 6 (Akulon K123) was supplied by La Seda S.A.

Pellets of both polymers were dried in an oven at 120°C during 24 h. Blending was carried out in a Haake Rheocord System 90 equipped with a 60 g mixing head. The temperature was set at 290°C and the rotor speed at 50 rpm. Mixing was performed for 5 min, until the torque became stabilized. Eleven compositions of Nylon 6/Vectra A, blends were prepared, in ratios of 100/0, 99/1, 98/2, 95/5, 90/10, 85/15, 70/30, 50/50, 30/70, 15/85 and 0/100 by mass.

The thermal stabilities of the blends were subjected to thermogravimetric analysis under dynamic and isothermal conditions with a Mettler TA-4000 TG-50 thermobalance. Samples were analysed as obtained directly from the Haake Rhecord System; the sample mass was around 10 mg in all cases. All experiments were carried out in an oxygen atmosphere (150 ml min^{-1}). The thermogravimetric analyses under dynamic conditions were carried out at a heating rate of 20°C min^{-1}. The percentage and the rate of mass loss were recorded as functions of temperature.

The isothermal analysis was performed at temperatures 10–50°C below the initial decomposition temperature, T_i. The samples were heated at a heating rate of 20°C min^{-1} from room temperature to a temperature 5°C lower than the desired temperature, and the heating rate was then reduced to 1°C min^{-1} in order to reach the isothermal temperature without overheating the samples. The blends were held at this constant temperature until a 2% conversion was obtained.

Results and discussion

The integral and differential degradation curves obtained for the individual polymers (Nylon 6 and Vectra A) and their blends are shown in Figs 1 and 2. The resulting data were completely reproducible, indicating anhomogeneous dispersion of both components in the blends. The thermoxidative degradation of Vectra A starts at 393°C and two degradation steps are observed. In the first step of degradation, the percentage mass loss is 41%, while 59% is observed in the second step. The mechanisms of Vectra A950 degradation were previously investigated by Hummel *et al.* [16], using a linear temperature-controlled pyrolysis technique with electron impact mass and FTIR spectrometers. At the beginning of the degradation processes, oxynaphthoyl and a series of hetero fragments containing one oxynaphthoyl unit and one or two oxybenzoyl units were detected, together with oxybenzoyl monomer and oligomers. At a higher temperature, corresponding to the maximum degradation rate in the first step, the formation of phenol, CO_2, CO and oxybenzoyl was observed. The predominant degradation mechanism involved chain fragmentation, accompanied by decarboxylation, decarbonylation and dehydration. At a temperature close to that of the second maximum degradation rate, decarbonylation overtook decarboxylation and most of the ester structures disappeared. On the other hand, diaryl ketone, dibenzofuran and fluorenone compounds were identified in the corresponding residues.

The process of Nylon 6 degradation has been widely investigated due to its technological applications in fibre production [17–26]. It also occurs in two steps, but degradation starts at a lower temperature (310°C) and the average mass loss associated with the second step is only 12%. It has been reported that the degradation of Nylon 6 leads to caprolactam and chain fragments with nitrile and

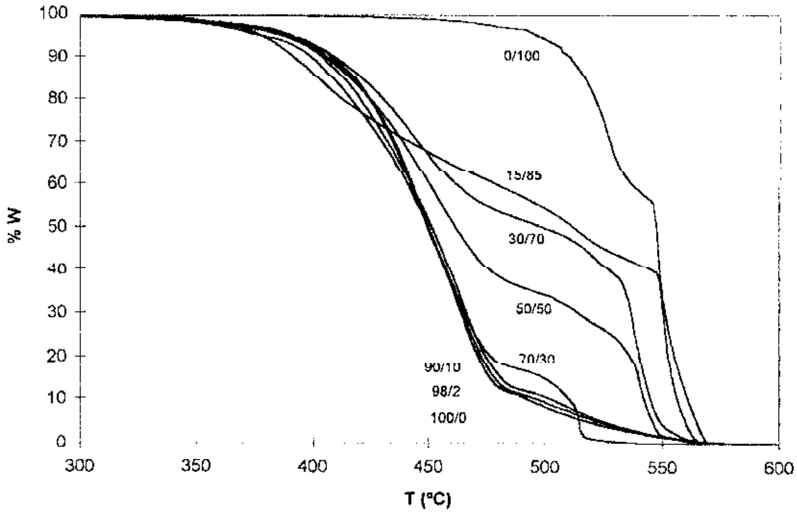

Fig. 1 TG curves for Nylon 6/Vectra A blends of different compositions

carbon–carbon unsaturated chain ends, together with a small amount of gaseous volatiles containing CO_2 and negligible amounts of CO and NH_3 [17, 18]. Nevertheless, different degradation mechanisms have been proposed in the literature: homolytic cleavage of alkylamide bonds [19–21], intermolecular exchange [22], *cis* elimination [23] and unzipping from carboxylic chain ends [24–26].

As evidenced by the thermogravimetric data, the thermal stability of the LCP is much better than that of Nylon 6. The thermogravimetric curves of the pure components were recorded before and after the mechanical blending in order to discard oxidation or crosslinking reactions due to degradation processes during blend preparation. The corresponding curves of the blends with low Vectra A contents are very similar to those registered for Nylon 6. However, the TG and DTG diagrams obtained for the blends with more than 15% of Vectra A indicate that the degradation behaviour of both individual polymers is retained in the corresponding blends. These thermogravimetric curves also show that the mass loss from these blends decreases as the LCP content increases, thereby demonstrat-

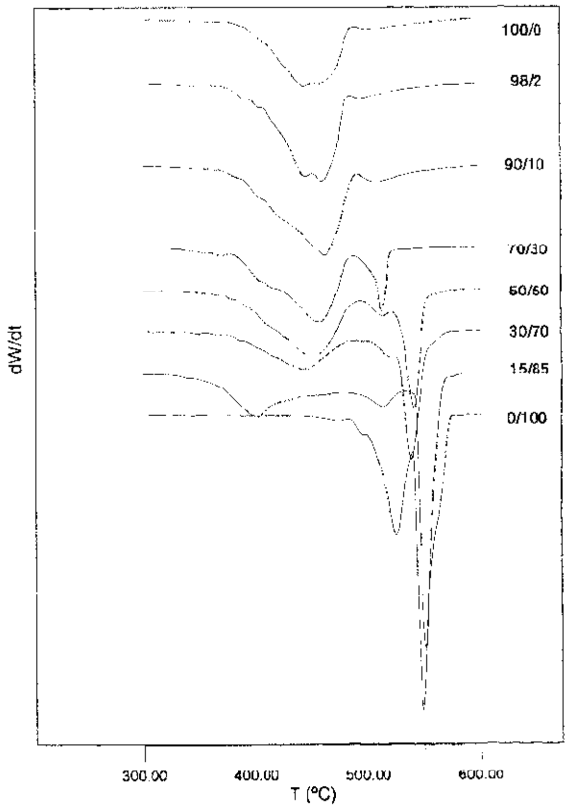

Fig. 2 DTG curves for Nylon 6/Vectra A blends of different compositions

ing that the thermal stabilities of the blends progressively improve with the addition of LCP.

It has been reported that interaction effects related to the blending process can either stabilize or destabilize the thermal behaviour of individual polymers [5]. In order to clarify this point, the experimental TG curves obtained for all blend compositions were compared with the theoretical ones. The latter were predicted from the mass loss data for the individual polymers and represent the behaviour expected for the blends in the absence of any interaction.

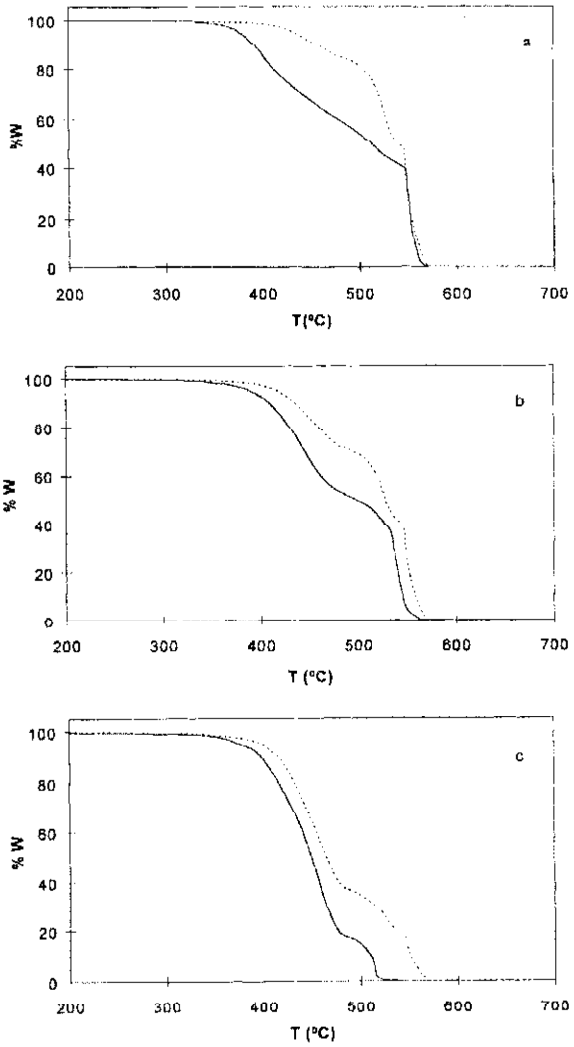

Fig. 3 Experimental (—) and calculated (·····) TG curves obtained for Nylon 6/Vectra A blends at the following compositions: (a) 15/85, (b) 30/70, (c) 70/30

As shown in Figs 3 and 4 for several blend compositions, the experimental and calculated curves did not coincide, indicating that some kind of interaction was taking place. For all the studied blends, the experimental mass loss was higher than the calculated value. This effect is particularly evident for blends with low contents of Nylon 6 (Fig. 3).With higher amounts of polyamide, both curves were very similar and only slight differences were observed in the upper temperature region (Fig. 4). These results indicate that the less stable polymer (Nylon 6) causes destabilization of the more stable Vectra A, while the degradation behaviour of the former is not strongly affected by the blending process. Analogous results have been observed for other polymer blends [5, 8], and have been justified in terms of the effects of the degradation products of the less stable polymer on the processes of degradation of the more stable one [7].

Analysis of the characteristic degradation temperatures confirms the results described above. The corresponding plots of the initial degradation temperature, T_i, and the temperatures of 10% and 50% mass loss, T_{10} and T_{50}, are shown in Fig. 5 as functions of the blend composition. It is seen that the experimental data are always lower than those expected from the proportions of the two components, except for the blends with low concentrations of Vectra A, for which simi-

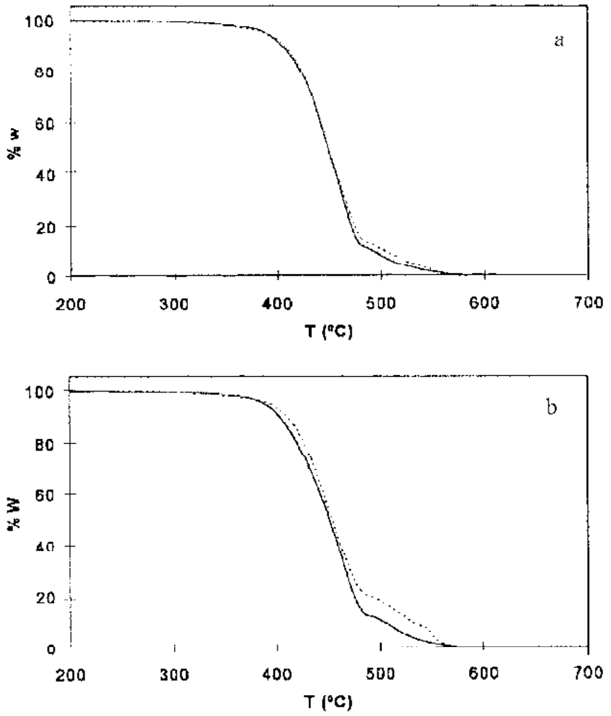

Fig. 4 Experimental (—) and calculated (·····) TG curves obtained for Nylon 6/Vectra A blends at the following compositions (a) 98/2, (b) 90/10

lar values were observed. Increasing amount of Vectra A decreases and levels off the characteristic T_i and T_{50} values, followed by increases in these temperatures with the addition of 70% of LCP. Analogous behaviour has been observed for other polymer blends [6] and a correlation has been made with the compatibility of the systems [6, 11].

On the other hand, it was observed that the temperature corresponding to the maximum rate of Vectra A degradation shifted to lower temperatures as the concentration of Nylon 6 in the blend increased. These data are shown in Fig. 2 and

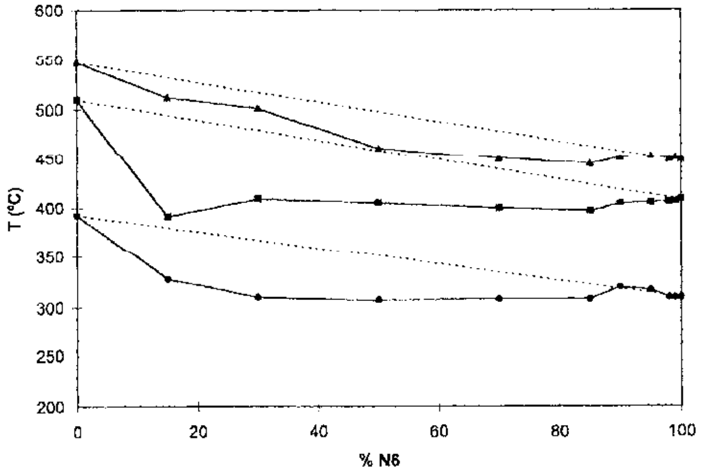

Fig. 5 Plots of characteristic degradation temperatures *vs.* the composition of the blends: • – T_i; ▪ – T_{10}; ▲ T_{50}

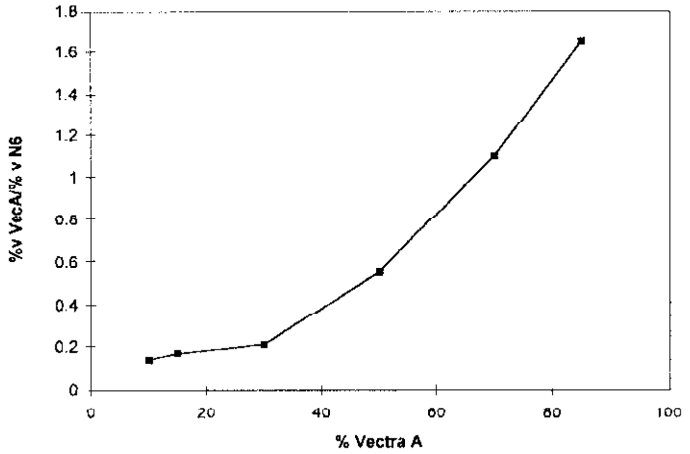

Fig. 6 Relative mass loss percentage *vs.* concentration of Vectra A in the blends

can be related to the destabilization effect of Nylon 6 on the degradation behaviour of Vectra A described before.

The mass losses associated with the different degradation steps are also function of the blend composition. The relative change in the mass loss percentage corresponding to the processes of Vectra A and Nylon 6 degradation is plotted *vs.* the concentration of Vectra A in the blends in Fig. 6. Increasing amount of Nylon 6 leads to a higher mass loss in the first step, while the second step, associated with Vectra A, is decreased. The mass loss ratio for the two stages shows an exponential increase with the concentration of Vectra A in the blends, as seen in Fig. 6. This is not only a consequence of the blend composition, but must also be related to the destabilization of Vectra A due to the presence of Nylon 6.

In order to confirm these results, the activation energies were analysed from the dynamic TG curves by using the approximative method developed by McCallum and Tanner [27], based on a function $F(c)$, which depends on the order of the reaction and the quantity of unreacted residue. It is important to remark that this is an approximative method and the energy values obtained have been used only for comparative purposes in order to analyse the effect of the blend composition.

The integrated rate equation is expressed as:

$$\log F(c) = \log\frac{AE_a}{\beta R} - 0.48E_a^{0.44} - \frac{0.45 + 0.22E_a}{T\cdot 10^{-3}} \quad (1)$$

where c is the fraction decomposed at time t, A is the frequency factor and E_a is the activation energy. For a first-order process, the function $F(c)$ is given by

$$F(c) = \ln\frac{1}{1-c} \quad (2)$$

Thus, plots of $\log(\ln(1/(1-c))$ *vs.* $1/T$ give a series of straight lines, confirming a first-order degradation kinetics for all the studied samples. The activation energy values were obtained from the slopes and were compared with the weighted average values predicted from the E_a data on the individual polymers in Fig. 7. It can be observed for the low Vectra A content blends that the E_a values are slightly higher than that obtained for pure component Nylon 6 and very similar to the theoretical values. When the amount of Vectra A is increased to more than 15%, an important reduction of the activation energy is observed. On the other hand, the higher the amount of liquid crystal, the larger the difference between the experimental and predicted E_a values.

The degradation of both pure components and the 70/30 Nylon 6/Vectra A blend were also analysed isothermally, at temperatures of 350, 360, 370 and 380°C for Vectra A, and at 260, 270, 280, 290 and 300°C for the other systems, using the Arrhenius approximation [28]. Analysis of the logarithm of the conversion against time for the 0–2% conversion range leads to a linear plot, as is expected for a first-order process. The rate constants, K, were obtained from the

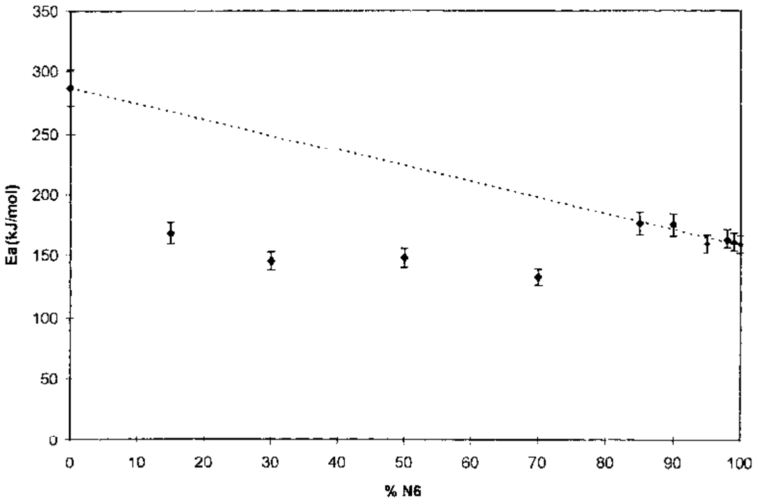

Fig. 7 Plots of experimental (◆) and theoretical (·····) activation energy values *vs*. blend compositions. (5% error bars are introduced as the experimental values were obtained by using the approximative method described in the text)

corresponding slopes, and the Arrhenius expression indicated below was used to obtain the values of the activation energy, E_a, and frequency factor, A:

$$K = A\exp - \frac{E_a}{RT} \tag{3}$$

In spite of the fact that isothermally determined E_a values are lower than those obtained in the dynamic experiments for all the blend compositions, they follow the same pattern. As an example, the energy values obtained by using the Arrhenius approximation are, respectively, 162 kJ mol^{-1} and 78 kJ mol^{-1} for the pure Vectra A and Nylon 6 components, and 81 kJ mol^{-1} for the 70/30 Nylon 6/Vectra A blend. It is clear from these data that the activation energy of the liquid crystal is reduced in the presence of Nylon 6 in a similar ratio in both dynamic and isothermal experiments.

These data agreed with the results described above, as the stability of Vectra A is gradually reduced by the addition of polyamide while the decomposition of Nylon 6 is not strongly affected by the blending process. It has been reported for several polymer blends [7] that, when the degradation of the less stable polymer starts, some molecular fragments can be transferred to the phase richer in the more stable polymer and this phenomenon leads to a reduction of the apparent activation energy associated with the degradation of the more stable polymer. Moreover, in other Nylon 6/ABS blends [11], the lower activation energy of some blend compositions were interpreted in terms of optimum interaction and miscibility between the two components.

Preliminary results obtained for Nylon 6/Vectra A blends by DSC and X-ray diffraction indicated that large amounts of Vectra A in the blends cause an important depression in the thermal transition temperatures of Nylon 6, together with changes in the crystalline structure. This behaviour must be related to the better compatibility and improved interfacial adhesion between the phases for these compositions. This enhances the diffusion of the degradation products of the less stable Nylon 6 in the Vectra A – richer phase, provoking destabilization of the LCP, as confirmed by the thermogravimetric data described in this paper. For this reason, further analysis will be carried out, using chromatography and mass spectrometry in order to investigate the mechanism of degradation of these systems.

Conclusions

The effects of the blending process on the thermal stabilities of Nylon 6/Vectra A blends were analysed. The thermogravimetric data provided evidence that the thermal stabilities of the Vectra A is much better than that of Nylon 6, and the thermal stabilities of the blends are progressively improved by the addition of the LCP.

Comparison of the theoretical and experimental thermogravimetric curves revealed that the experimental mass loss values were higher than those calculated for the blends with high Vectra A contents, indicating that some kind of interaction was taking place.

This behaviour was confirmed by the analysis of thermogravimetric parameters such as characteristic degradation temperatures, relative mass loss and activation energies as a function of blend composition. The thermogravimetric data demonstrated that Nylon 6 was not strongly affected by the blending process, but caused destabilization of the more stable Vectra A. This effect is particularly evident as the amount of Vectra A in the blends increases, and must be related to an improvement in the interfacial adhesion between the two phases for these blend compositions.

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