THERMAL STUDY OF BLENDED SYSTEMS OF NYLON 6 AND A LIQUID

CRYSTALLINE POLYESTER

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SUMMARY
    The thermal properties of solution-prepared blends of nylon 6
and the liquid-crystalline polyester poly(biphenyl-4,4'-ylene
sebacate) have been studied by differential scanning calorimetry.
The results show that a rather strong interaction between the
two polymers does really exist.

INTRODUCTION

    The melting behaviour of nylon 6 has been extensively studied
by dilatometry (1,2), differential thermal analysis (3,4) and
calorimetry (5). The effect of the kinetics of crystallization
of some nucleating agents, including the other component of a
polymer blend, has also been investigated (2,6).

    Blends of commercial polymers and copolymers have been studied
on several occasions over the years with a view to their possible
use in industry. Nylon 6 is capable of specific interactions when
blended with other polymers, owing to its amide groups; neverthe-
less, compatible polymer blends containing polyamides are rarely
referred to in the literature (7).

    The liquid crystalline main-chain polymers (LCP), with their
peculiar structure and properties, seem to be very promising when
blended with commercial polymers. The thermomechanical and calo-
rimetric behaviour of blends of commercial polymers with LCP has
recently been examined. Kiss (8) has found that the mechanical
properties of a commercial polymer can be improved by the addition
of an LCP, which forms elongated domains parallel to the flow

direction during processing. The calorimetric studies published
so far (9,10) indicate that significant interactions between the
two components of the blends take place, even in the absence of
miscibility.

In this paper we describe the results of a calorimetric study
of blends of nylon 6 with a liquid crystalline thermotropic poly-
ester, poly(biphenyl-4,4'-ylene sebacate)(PB8).

EXPERIMENTAL

Nylon 6 was a commercial polymer with an inherent viscosity
of 215 cm^3/g as measured at 298 K in a phenol-tetrachloroethane
solution (c=0.005 g/cm^3). PB8 was prepared as reported else-
where (9). Several blends containing 4 , 5.6 , 8 , 10 , 12 , 17 ,
20 , 25 and 50 percent of PB8 were obtained by coprecipitation
in methanol from phenol-tetrachloroethane solution 60:40 (w:w)
and dried in vacuo at 313 K for 72 hours.

Homopolymers and blends were examined by differential scanning
calorimetry, using samples with the same thermal history to pro-
vide a valid comparison. Calorimetric analysis was carried out
in a DSC4 Perkin Elmer apparatus. Each sample was heated at
10 deg/min up to 563 K to obtain the complete isotropization of
PB8. This temperature exceeds the equilibrium melting temperature
of nylon 6 (557 K) and is considered sufficient to destroy its
crystallization nuclei completely (11). After being held at 563 K
for a few seconds under nitrogen, the samples were cooled to room
temperature at 10 deg/min and the relevant cooling traces were
registered. These samples, as well as similar samples quenched
from 563 K with a nominal rate of 320 deg/min , were reheated
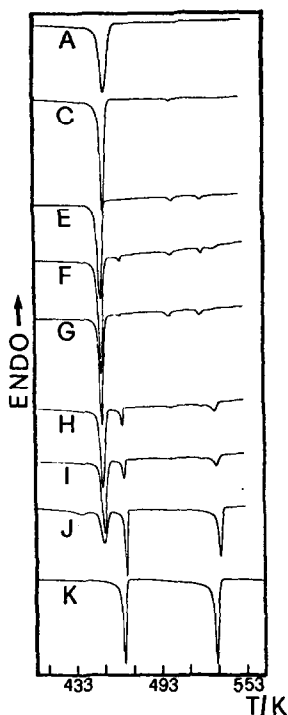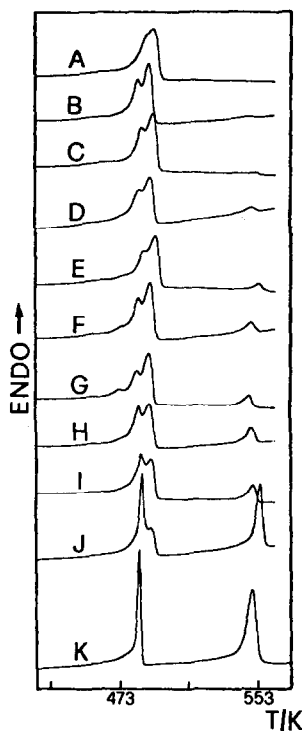at 10 deg/min and the DSC traces were recorded.

Fig. 1   Fig. 2

Fig. 1. DSC cooling traces (scan rate 10 deg/min) of nylon 6 (A),
PB8 (K) and (C),(E),(F),(G),(H),(I),(J),blends containing 5.6 ,
10,12,17,20,25,50 % PB8 respectively, from the melt.

Fig. 2. DSC heating traces (scan rate 10 deg/min)of nylon 6 (A),
PB8 (K) and (B),(C),(D),(E),(F),(G),(H),(I),(J), blends containing
4,5.6,8,10,12,17,20,25,50 % PB8 respectively, cooled from 563 K
at 10 deg/min to room temperature.

RESULTS AND DISCUSSION

   Fig.1 displays the thermograms of the homopolymers and blends
cooled from 563 K at 10 deg/min, whereas Fig.2 shows the reheating
traces. Previous studies (9,12) had shown that pure PB8 shows two
distinct sharp endotherms on heating (curve K fig.2). The lower
temperature effect has been associated with a crystal-to-smectic
transition and the high temperature one with a smectic-to-isotrop-
ic transition. The reverse transitions are observed in the cooling

traces   as sharp exotherms (curve K Fig.1).

Nylon 6 shows a single, well-resolved exotherm on cooling, cen-
tered at 459 K (curve A Fig.1). The heating trace is characterized
by an endotherm peaking at 493 K with a slight indication of a low
temperature shoulder. A well-resolved two-peak pattern was never
observed with any of the thermal treatments investigated in this
study, contrary to published statements (13).

The heating traces of the blends show three endotherms; that
located at 543 - 553 K can certainly be associated with the iso-
tropization of the PB8 component. This transition, if the composi-
tion is taken into account, appears almost independent of the
nylon content. The two main peaks of fusion at ca. 483 and 493 K
can be attributed to the melting of PB8 and nylon 6 respectively,
at least for the samples with PB8 content above 17%. A low temper-
ature shoulder of these peaks can be observed for all samples; for
the 17% blend this is resolved as a peak centered at 471 K. This
low-temperature shoulder can be attributed to premelting phenomena.
The temperature of the main melting peak of nylon remains approx-
imately constant or decreases slightly on blending nylon with
increasing amounts of PB8.

In the case of blends with low PB8 content, the first transition
(ca. 480 K) cannot be simply attributed to the fusion of a separate
PB8 phase, owing to its intensity.

The 5.6% blend was annealed to examine this behaviour in greater
detail. Virgin samples were cooled from 563 K at 10 deg/min ,
reheated to 473 K and held at this temperature for different times
before being cooled at 10 deg/min to room temperature and scanned
up to 563 K.

It can be seen from Fig.3 that a longer annealing time is follow-
ed by a gradual increase in the intensity and sharpness of the
first peak (485 K), whereas the higher temperature peak (493 K)
undergoes a strong intensity reduction and then finally disappears.
This behaviour is due probably to a morphological change in the
blend as a result of the annealing treatment, since the heating

traces for the same samples after cooling from 563 K at 10 deg/min are almost carbon copies of that obtained for the unannealed blend. This confirms that, as anticipated, the endotherm observed at 485 K in the heating trace of this blend (curve C Fig.2) is to be associated with the fusion of nylon crystals whose habit is different to that of those in the pure nylon sample.
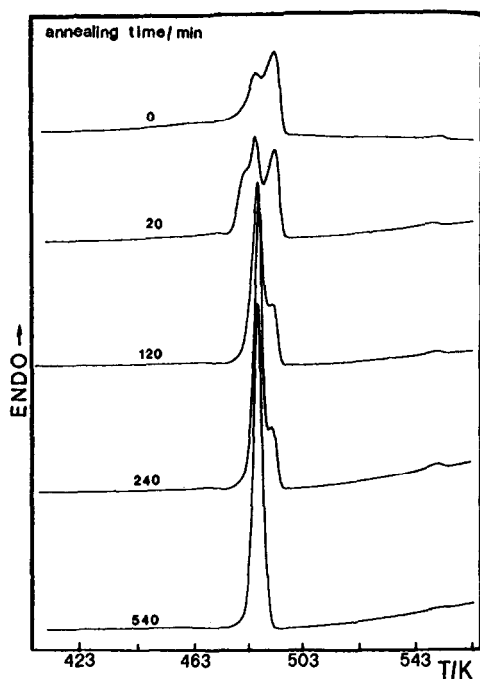

Fig. 3. DSC heating traces of 5.6% blend annealed at 473 K for the indicated times.

A rather strong interaction between the two polymers must thus be envisaged if the presence of a PB8 phase influences the crystallization of nylon.

The blend cooling traces are collected in Fig.1. It is apparent from the crystallization exotherms of the nylon phase that this is only slightly affected by the PB8 content.

As far as the transitions connected with the PB8 component are concerned, a peculiar behaviour is found for blends with about 4 to 25% PB8. An increase through this range results in a gradual

decrease in the intensity of the two exotherms at ca. 533 and
468 K associated with the formation of a smectic phase and the
crystallization of the PB8 component respectively. The simulta-
neous development of the two new exotherms centered at ca. 523
and 503 K can be seen.

The thermal program illustrated in Fig. 4 was used to assess
the reproducibility of this behaviour. The heating (cooling) rate
of 10 deg/min was always used to study the thermal behaviour
of a 10% blend sample. Every leg of this program was registered.
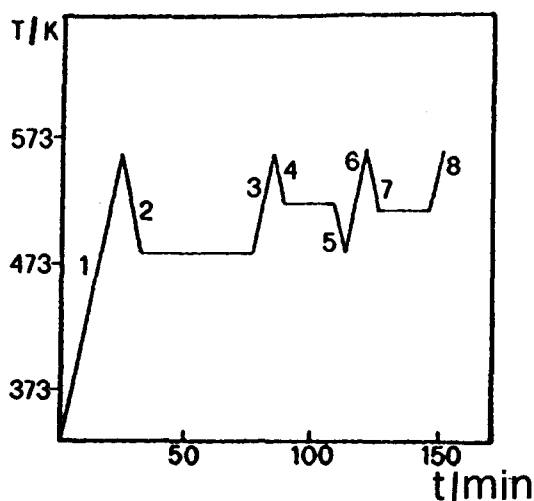

Fig. 4. Thermal program used for DSC and heat treatment of 10%
PB8 blend.

The DSC traces (Fig.5) clearly show that the reproducibility
of this behaviour is satisfactory. Whatever the previous thermal
treatment, a single endotherm on heating and two exotherms on
cooling are observed, accompanied by very small changes in the
transition. Moreover the enthalpy change associated with the
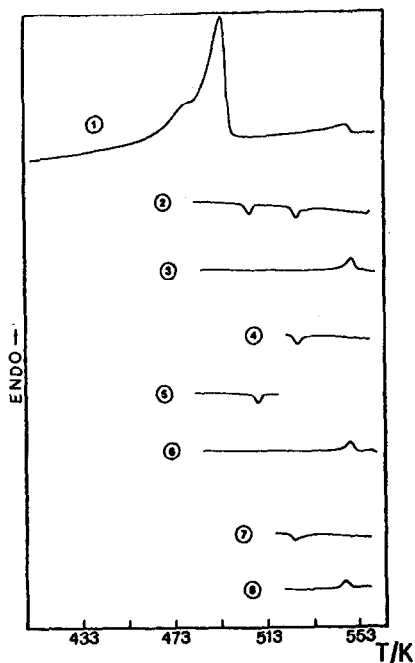endotherm corresponds approximately to the sum of the enthalpies
of the two exotherms.

Fig. 5. Thermograms of 10% PB8 blend at 10 deg/min and scanned according to the thermal program in Fig. 4.

To our knowledge, such a behaviour has never been observed in mesomorphic systems. It would be desiderable to further clarify this point by other techniques besides calorimetry. Unfortunately, the transitions detected by DSC are not accompanied by signifi-cant changes in the optical characteristics, as observed by polarizing microscopy.

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