

# Structure–Microhardness Correlation in Blends of Nylon 6/Nylon 66 Monofilaments

M. E. CAGIAO,<sup>1</sup> F. ANIA,<sup>1</sup> F. J. BALTÁ CALLEJA,<sup>1</sup> M. HIRAMI,<sup>2</sup> T. SHIMOMURA<sup>2</sup>

<sup>1</sup> Instituto de Estructura de la Materia, CSIC, Serrano 119, 28006 Madrid, Spain

<sup>2</sup> Unitika Ltd., Research and Development Center, 23 Kozakura, Uji, Kyoto 611-0021 Japan

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**ABSTRACT:** The microstructure (crystallinity, long spacing) and the micromechanical properties (microhardness  $H$ ) of two series of nylon 6 and nylon 66 monofilaments and their blends were investigated as a function of annealing temperature  $T_A$  and uniaxial deformation in a wide composition range. In case of the homopolymers, the gradual rise of microhardness with  $T_A$  is interpreted in the light of the increasing values of the crystallinity  $\alpha$  and the hardness of the crystals  $H_c$ . The depression of the hardness values of the blends from the additive behavior of the hardness of individual components is discussed in the basis of the crystallinity depression of one component by the second one and viceversa. Finally, the influence of drawing and pressing the blends at 130°C which leads to a hardness increase is also explained in the light of an increase in the  $H_c$  value of nylon 66 due to orientation. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 636–643, 2000

**Key words:** crystallinity; long spacing; microhardness; nylon 6; nylon 66; monofilaments; homopolymers; blends; annealing temperature; uniaxial deformation

## INTRODUCTION

The scientific and technological relevance of polyamides is well known, the textile industry being one of their main fields of application. Polyamides are also increasingly used as matrix materials in the production of fiber reinforced composites. Among all the aliphatic polyamides, nylon 6 and nylon 66 are the most widely used. Although both polymers are relatively similar from a structural point of view, the use of blends of both nylon 6 and nylon 66 presents some advantages. For example, composite fibers made of blends with a definite

concentration of terminal groups show better dyeability than nylon 66 and an improved storage stability in moist conditions than nylon 6.<sup>1</sup>

It is now well established that the mechanical properties of semicrystalline polymers depend, to a large extent, on their morphology, and the latter can be modified by using different processing conditions: temperature, pressure, etc.

Microhardness is becoming a very important technique in polymer characterization. This is so because it provides a bridge between macroscopic mechanical properties, such as yield stress<sup>2</sup> and some microstructural characteristics in polymers: crystal size,<sup>3</sup> crystallinity,<sup>3,4</sup> etc. Recently, the microhardness technique was also shown to be useful in determining the glass transition temperature  $T_g$  in amorphous polymers,<sup>5</sup> and in detecting polymorphic changes in semicrystalline polymers.<sup>6</sup> It has also been successfully used to

Correspondence to: F. J. Baltá Calleja.

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detect precrystallization states in poly(ethylene terephthalate) (PET) crystallized from the glassy state.<sup>7</sup> Although microhardness has been widely used in the characterization of many polymer systems,<sup>8–10</sup> still its application to polyamides is relatively scarce.<sup>11–13</sup>

The aim of this work is to investigate the effect of both annealing temperature and uniaxial mechanical drawing on the structure and the mechanical properties of nylon 6 and nylon 66 blends. In the first part of the work, we will show the influence of the annealing temperature on the properties of two series of filaments constituted by nylon 6 and nylon 66 homopolymers, respectively. In the second part, we will discuss the behavior of filaments made of blends of nylon 6 and nylon 66 with different composition. The filaments were drawn to  $\lambda = 3$ , followed by pressing in a hot-roller at  $T_A = 130^\circ\text{C}$ . The latter annealing temperature coincides with the beginning of the “Brill transition” region (130–230°C) in nylon 66.<sup>14</sup> The latter is a transition from a triclinic to a pseudohexagonal unit cell.<sup>15</sup>

We have carried out this study at room temperature and under ambient conditions. It is important to stress this point, because of the extreme sensitivity of polyamides to moisture. It is well known that water, even in a very small amount, has a plasticizing effect on these materials. For instance, the microhardness of a previously dried polyamide exponentially decreases as a function of time when being exposed to the atmospheric moisture.<sup>11</sup>

## EXPERIMENTAL

### Materials

The nylon 6 and nylon 66 samples used in this study were furnished by Unitika (Japan). Most of them were semitransparent filaments of circular cross section (diameter  $\cong 1.1$  mm). Those samples previously drawn to  $\lambda = 3$  and pressed in a hot roller at  $T_A = 130^\circ\text{C}$  had rectangular cross sections of about  $1 \times 0.32$  mm<sup>2</sup>.

Filaments of both nylon homopolymers were annealed for 3 h at different temperatures  $T_A$ . We have studied the influence of  $T_A$  on the crystallinity, long spacing, and microhardness. Nylon 6 was annealed at 130, 180, 200, and 210°C. Nylon 66

filaments were heated at 130, 180, 200, 210, 220, 230, and 240°C.

We studied, as well, three series of filaments made of blends of nylon 6/nylon 66 having the following weight compositions: 100/0, 70/30, 50/50, 30/70, and 0/100. In the first series, the samples are simply “as spun” filaments—that is, they did not receive any thermal treatment. In the second series filaments were annealed at  $T_A = 130^\circ\text{C}$  for 3 h. Finally, in the third series filaments were drawn to  $\lambda = 3$  and then pressed in a hot roller at  $T_A = 130^\circ\text{C}$ . We investigated the influence of the composition, the annealing process and the drawing of the samples on their microstructure and mechanical properties.

### Techniques

Samples were analyzed by differential scanning calorimetry (DSC) using a Perkin-Elmer differential scanning calorimeter DSC 7. The typical sample weight was 5 mg and the heating rate 20°C/min. All the scans were performed in a N<sub>2</sub> atmosphere.

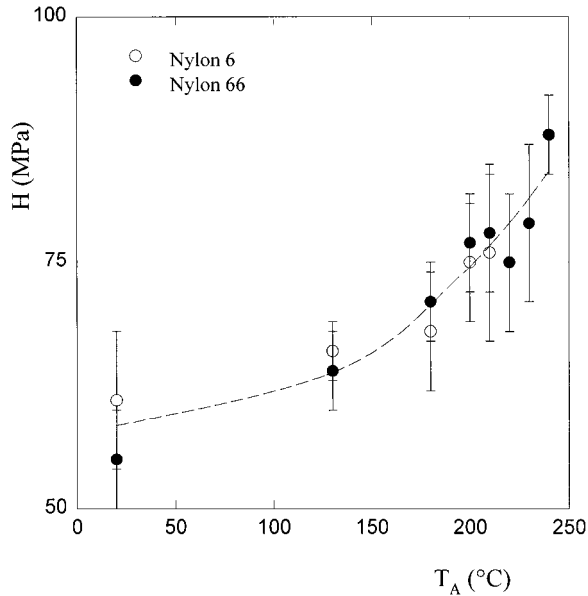
Crystallinity values  $\alpha$  have been derived from the melting enthalpy data obtained by DSC using the following formula:

$$\alpha = \frac{\Delta H_m}{\Delta H_m^\infty} \quad (1)$$

where  $\Delta H_m$  is the experimental melting enthalpy and  $\Delta H_m^\infty$  is the melting enthalpy for an infinitely long crystal. From the literature, we have taken  $\Delta H_m^\infty = 55.2$  cal/g for nylon 6,<sup>16</sup> and  $\Delta H_m^\infty = 61$  cal/g for nylon 66.<sup>17</sup>

A Rigaku Denki diffractometer RAD-rB with graphite monochromator was used to obtain small-angle X-ray scattering (SAXS) patterns, using a CuK $\alpha$  radiation source from a rotating anode working at 50 kV and 200 mA. A small angle goniometer with linear collimators was used, being the dimensions of the first and the second slits  $12 \times 0.5$  and  $12 \times 0.3$  mm<sup>2</sup>, respectively. The sample-detector distance was 300 mm.

Microhardness ( $H$ ) was measured at room temperature using a Leitz tester equipped with a square-based diamond indenter. The  $H$  value was derived from the residual projected area of indentation according to the expression  $H = kP/d^2$  (MPa), where  $d$  is the length of the impression diagonal in meters,  $P$  is the contact load applied in  $N$ , and  $k$  is a geometrical factor equal to 1.854



**Figure 1** Plot of hardness for nylon 6 (open symbols) and nylon 66 (solid symbols) monofilaments with annealing temperature  $T_A$ .

$\times 10^{-6}$ . A loading cycle of 0.1 min and loads of 0.25, 0.5, and 1 N were used. A minimum of ten indentations was performed on each sample, and all the results were averaged. Both diagonals (parallel and perpendicular to the fiber axis) were measured, except in the samples that had been drawn and pressed in a hot roller. In these last samples only the diagonal parallel to the fiber axis could be clearly seen and measured. The other filaments did not show any anisotropy.

## RESULTS AND DISCUSSION

### Structure and Microhardness of the Homopolymers

Figure 1 shows the evolution of the microhardness  $H$  as a function of the annealing temperature  $T_A$ . This evolution is similar for both nylon 6 and nylon 66 homopolymers.  $H$  increases with  $T_A$  following an Arrhenius-type equation:

$$H = H_0[1 + m \cdot \exp[n/(T_A + 273)]] \quad (2)$$

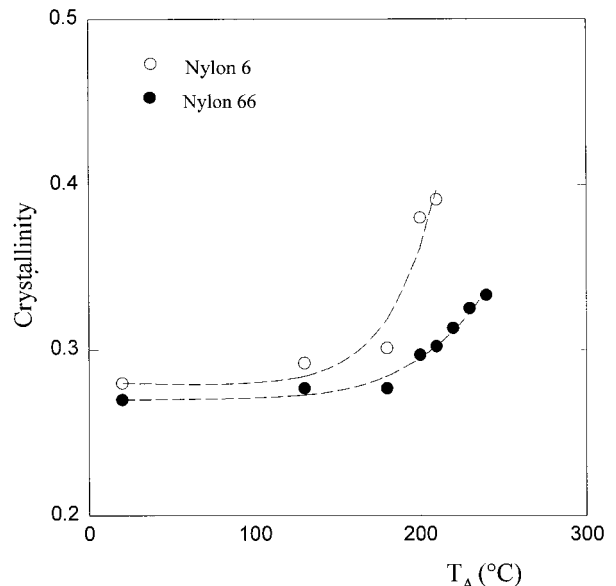
In this formula,  $H$  and  $H_0$  are the hardness values at the temperature  $T_A$  and at room temperature, respectively, and  $m$  and  $n$  are constants.

All samples show hardness values between 60 MPa (nontreated filaments) and 90 MPa (nylon 66 annealed at 240°C). It is noteworthy that the present values are much lower than those reported in the literature for non-annealed samples, i.e., 90 MPa for nylon 6,<sup>18</sup> 80–120 MPa for nylon 66,<sup>19, 20</sup> or 152 MPa for the injection molded materials.<sup>12</sup> At the moment, we have no explanation for the small hardness values found in the present study.

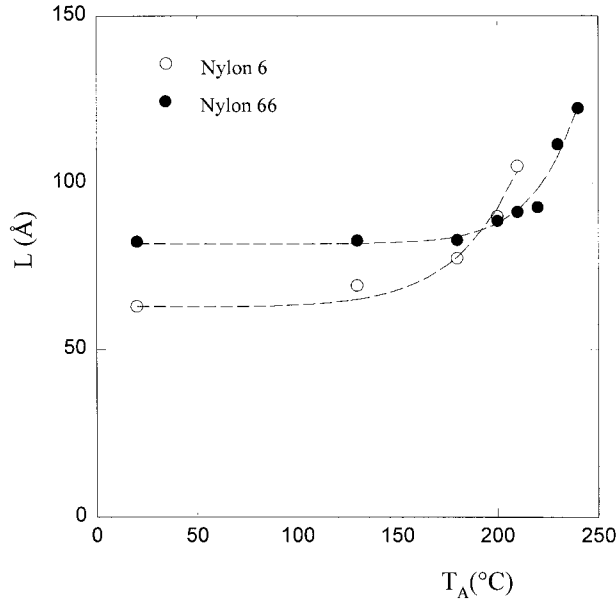
Figure 2 shows the crystallinity dependence with  $T_A$  for both kinds of filaments. All samples show relatively low crystallinity values, between 28 and 40%. It is clear that nylon 6 reaches crystallinities higher than those of nylon 66, particularly for  $T_A \geq 130^\circ\text{C}$ .

The long spacing  $L$ , calculated from the peak position in the SAXS diagrams, increases with  $T_A$  for both series of filaments (Fig. 3). Nylon 66 samples show higher  $L$  values than those of nylon 6 for  $T_A < 210^\circ\text{C}$ , whereas for  $T_A > 210^\circ\text{C}$  the  $L$  values for the nylon 6 are the largest ones. This is due to the lower melting point of nylon 6. The molecular mobility of nylon 6 starts well before than the mobility of nylon 66.

It is important to note that the increase of both crystallinity and long spacing  $L$  with  $T_A$  (Figs. 2 and 3) also follows Arrhenius-type equations.



**Figure 2** Degree of crystallinity (derived from DSC) in nylon 6 and nylon 66 monofilaments as a function of annealing temperature  $T_A$ . (Symbols: same as in Fig. 1.)



**Figure 3** Long spacing  $L$  for nylon 6 and nylon 66 monofilaments vs. annealing temperature  $T_A$ . (Symbols: as in Figs. 1 and 2.)

By comparison of Figures 1 and 2, it can be concluded that the crystallinity evolution with  $T_A$  for both nylon 6 and nylon 66 is similar to that of microhardness. However, while the experimental hardness values are well described by a single equation, the crystallinities found for nylon 6 are always higher than the corresponding ones for nylon 66. As it is well known, assuming a two-phase model, hardness  $H$  in a semicrystalline polymer can be represented as<sup>19</sup>

$$H = H_c \alpha + H_a (1 - \alpha) \quad (3)$$

where  $H_c$  and  $H_a$  are the intrinsic hardness values for the crystalline and amorphous phases, respectively, and  $\alpha$  is the volume fraction of crystalline material. According to this analysis, as  $H^6 \cong H^{66}$  (see Fig. 1), and if we admit that  $H_a \ll H_c$  for both homopolymers, then the crystal hardness  $H_c$  values for nylon 6 are expected to be smaller than those for nylon 66. In this way  $H_c$  for nylon 6 would compensate its higher crystallinity and would give rise to similar  $H$  values, in agreement with the experimental results. Crystalline hardness  $H_c$  is related to crystal size  $l$  by the expression<sup>3</sup>

$$H_c = \frac{H_c^\infty}{1 + \frac{b}{l}} \quad (4)$$

where  $H_c^\infty$  is the crystalline hardness for an infinitely long crystal. The  $b$  parameter is defined by<sup>3</sup>

$$b = \frac{2\sigma_e}{\Delta h} \quad (5)$$

Here  $\sigma_e$  is the basal surface free energy, and  $\Delta h$  is the energy required for the plastic deformation of the crystals. From the literature, we have taken  $\sigma_e = 47$  erg/cm<sup>2</sup> for both nylon 6<sup>21</sup> and nylon 66.<sup>22</sup> We can then calculate the thermodynamic crystal size  $l_c$  of each sample by applying the Thomson-Gibbs equation to the calorimetric data:

$$T_m = T_m^0 \left( 1 - \frac{2\sigma_e}{\Delta H_m^\infty l_c} \right) \quad (6)$$

It is important to note that  $T_m$  does not change with the annealing temperature  $T_A$  in any of the homopolymers (see Table I). Introducing the  $\sigma_e$ <sup>21,22</sup> and  $\Delta H_m^\infty$ <sup>16,17</sup> values found in the literature, and taking  $T_m^0 = 260^\circ\text{C}$  for nylon 6<sup>23</sup> and  $H_m^0 = 301^\circ\text{C}$  for nylon 66,<sup>23</sup> we found that the thermodynamic crystal size  $l_c$  is almost identical for both homopolymers (42–45 Å), and does not depend on the annealing temperature  $T_A$  (see Table I). This is in agreement with the  $l_c$  values cited in the literature for nylon 6<sup>24</sup> and nylon 66<sup>25</sup> fibers annealed at different temperatures, in which the crystal size reaches a constant value of about 50 Å for annealing times  $t_A \geq 1$  s.<sup>25</sup>

**Table I** Filaments of Nylon 6 and Nylon 66 Homopolymers Annealed at Different Temperatures  $T_A$ <sup>a</sup>

Nylon 6			Nylon 66		
$T_A$ (°C)	$T_m$ (°C)	$l_c$ (Å)	$T_A$ (°C)	$T_m$ (°C)	$l_c$ (Å)
130	221.3	45	130	261.2	43
180	220.7	45	180	260.9	43
200	220.2	44	200	260.7	42
210	220.1	44	210	260.2	42
			220	260.2	42
			230	260.0	42
			240	260.1	42

<sup>a</sup>  $T_m$ : melting temperature;  $l_c$ : thermodynamic crystal size derived from  $T_m$  data (see text).

If  $l_c$  is identical for nylon 6 and nylon 66 and crystalline hardness  $H_c$  is higher for nylon 66, then, assuming  $b$  to have similar values for both homopolymers (eq. (4)), the crystalline hardness for an infinitely long crystal  $H_c^\infty$  ought to be also higher in the case of nylon 66.

On the other hand, if  $H_c$  increases with annealing temperature and  $l_c$  is kept constant, the only explanation for this behavior, assuming both  $H_c^\infty$  and  $\sigma_e$  to be constant, should be that  $\Delta h$  also increases with  $T_A$  due to the increasing perfection of the crystals.

Parallel to  $H$  and  $\alpha$ , the long spacing  $L$  also increases with annealing temperature in the two series of filaments (see Fig. 3) even if  $l_c$  does not change.

The  $H$  and  $\alpha$  increase with  $T_A$  while  $l_c$  is keeping constant could be explained if the crystals grow laterally. In fact, in ref. 24 Murthy et al. present the results obtained in the study of nylon 6 filaments annealed at different temperatures. Among other relevant results, the authors find that the crystal size in molecular direction  $l$  does not change as a consequence of the thermal treatment. However, the long spacing  $L$  increases with  $T_A$ . And what is more important, crystallite size along the  $a$  axis also increases with  $T_A$ . This lateral growth could also explain the behavior shown by our samples during the annealing process.

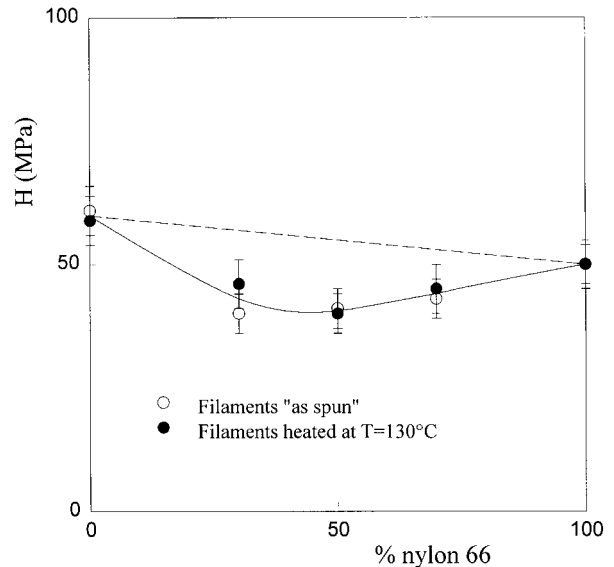
### Structure and Microhardness of Blends of Nylon 6 and Nylon 66: Influence of Composition

Figure 4 illustrates the influence of the composition on the hardness of the samples of the first series ("as spun" filaments) and of the second one (filaments annealed at 130°C for 3 h). Both series behave similarly. In other words, the annealing process at 130°C does not seem to affect the mechanical properties of the blends. The hardness of the intermediate composition filaments is however depressed below the values predicted by the additivity law:

$$H = H_1\Phi + H_2(1 - \Phi) \quad (7)$$

In this expression,  $H_1$  and  $H_2$  represent the individual hardness values of each component, and  $\Phi_1$  and  $(1 - \Phi_1)$  are their respective weight fractions. The hardness additivity law corresponds to the dashed line in Figure 4.

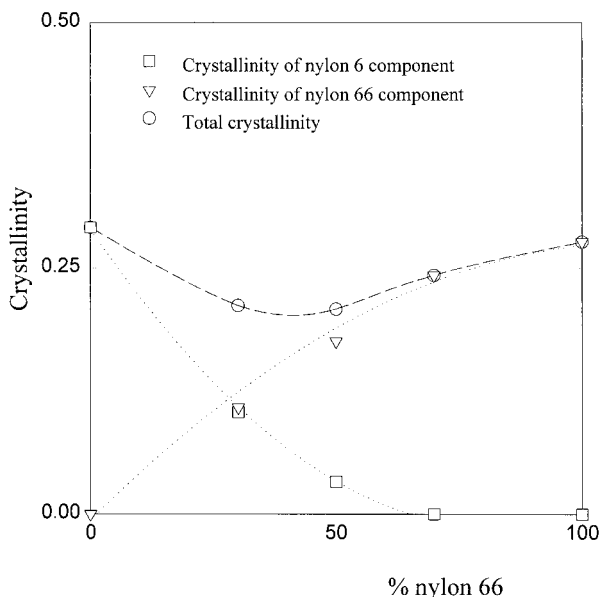
Figure 5 shows the crystallinity values as a function of the composition in the samples of the



**Figure 4** Hardness dependence on composition in blends of nylon 6 and nylon 66. Open symbols: "as spun" filaments. Solid symbols: filaments annealed at  $T_A = 130^\circ\text{C}$  for 3 h. Dashed line: additivity behavior from eq. (7).

second series (filaments annealed at 130°C for 3 h). The individual crystallinity values of each component in the blends are also included. We do not have information concerning the crystallinity values in the "as spun" filaments. However, from the similarity in the hardness values for the two series of blends (Fig. 4), we may assume that neither the hardness nor, probably, the crystallinity of the filaments is affected by the annealing treatment at 130°C. From the inspection of Figure 5, it is hence clear that each component of the blend has a depressing effect on the crystallinity of the other. And this depression is stronger in the case of nylon 66, i.e., in the thermogram of the sample of composition 30/70 only the melting peak corresponding to the nylon 66 appears. Additionally, the melting point of each component is lower than those corresponding to the homopolymers (see Table II). This is a clear indication that the crystals in the blends are of smaller size than those of the homopolymers (Table II). Therefore, the hardness depression in the filaments of intermediate composition can be explained by the combined effect of the lower crystallinity and the reduced crystal size of each component. The influence of the former is probably the most important factor.

Concerning the changes in long spacing  $L$  with composition, in both series  $L$  slightly increases



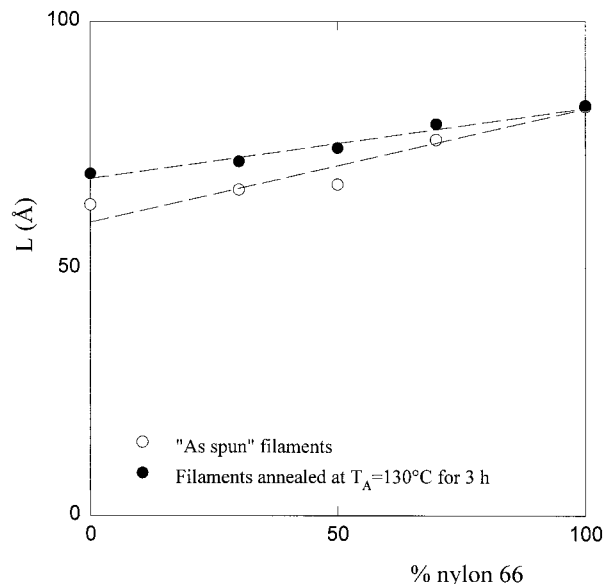
**Figure 5** Degree of crystallinity (derived from DSC) as a function of composition in blends of nylon 6 and nylon 66 annealed at  $T_A = 130^\circ\text{C}$  for 3 h. Symbols are as follows: □: crystallinity contribution of nylon 6 component; ▽: crystallinity contribution of nylon 66 component; ○: total crystallinity.

linearly with the nylon 66 content (see Fig. 6). There is a small but nevertheless detectable increase in the  $L$  value in going from the “as spun” filaments to the annealed series, i.e., from 63 to 69 Å for nylon 6. However, this difference gradually decreases with increasing amount of nylon 66, so that for the sample of composition 0/100, the  $L$  value for the filament after annealing does not vary. Again, this is due to the fact that  $130^\circ\text{C}$  does not

**Table II** Filaments of Blends of Nylon 6 and Nylon 66 with Different Composition Annealed at  $T_A = 130^\circ\text{C}$  for 3 h<sup>a</sup>

N6/N66	Nylon 6			Nylon 66		
	$T_m$ (°C)	$l_c$ (Å)	$\alpha$	$T_m$ (°C)	$l_c$ (Å)	$\alpha$
100/0	221	45	0.29	—	—	—
70/30	218	42	0.10	255	37	0.11
50/50	214	38	0.03	256	38	0.18
30/70	—	—	—	259	41	0.24
0/100	—	—	—	261	43	0.28

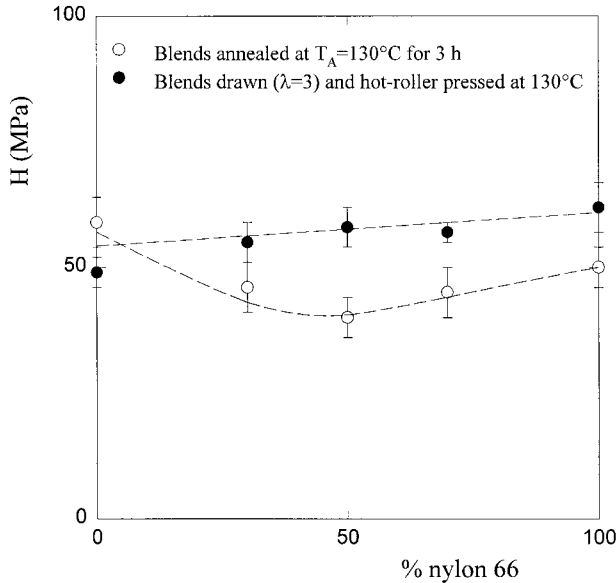
<sup>a</sup>  $T_m$ : melting temperature;  $l_c$ : thermodynamic crystal size of each component derived from  $T_m$  data.



**Figure 6** Long spacing  $L$  as a function of composition in blends of nylon 6 and nylon 66. Open symbols: “as spun” filaments. Solid symbols: filaments annealed at  $T_A = 130^\circ\text{C}$  for 3 h.

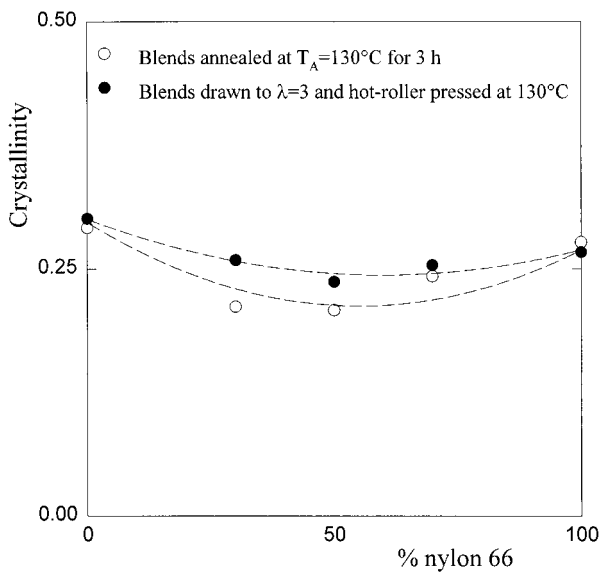
produce any rearrangement in nylon 66 while it does in nylon 6.

Let us next compare the behavior of the second series (samples annealed at  $130^\circ\text{C}$  for 3 h), and the third one (samples drawn to  $\lambda = 3$  and then pressed in a hot roller at  $130^\circ\text{C}$ ). Figure 7 shows the variation of hardness  $H$  with the composition of both series. In the series of drawn and pressed filament samples  $H$  increases with the content of nylon 66 following the hardness additivity law (eq. (7)). The hardness of nylon 6 does not change with deformation within experimental error and it can also be seen that  $H$  slightly increases due to the deformation process, i.e., from 50 to 62 MPa for nylon 66. The crystallinity (see Fig. 8) also experiences a small increase for the samples of intermediate composition (i.e., from 0.21 to 0.26 in the case of 70/30 sample), but not for the homopolymers. From the evolution of the crystallinity and the thermodynamic crystal size values (see Table III) with the composition, it can be deduced that in the drawn filaments each component hinders the crystallization capability of the other. Again, in the sample of composition 30/70, only the melting peak corresponding to the nylon 66 appears. Furthermore, it is clear that the drawing of the samples does not influence the crystal size of each component (compare  $l_c$  values



**Figure 7** Plot of hardness vs. composition in blends of nylon 6 and nylon 66. Open symbols: filaments annealed at  $T_A = 130^\circ\text{C}$  for 3 h. Solid symbols: filaments drawn to  $\lambda = 3$  and pressed in a hot roller at  $130^\circ\text{C}$ .

in Tables II and III). On the other hand,  $H$  increases with the nylon 66 content. However, the hardness of nylon 6 does not seem to change. This could be explained by an increase of the crystalline hardness  $H_c$  in the nylon 66 due to the fila-



**Figure 8** Degree of crystallinity as a function of the composition in blends of nylon 6 and nylon 66. Symbols are as in Figure 7.

**Table III** Filaments of Blends of Nylon 6 and Nylon 66 with Different Composition, Drawn to  $\lambda = 3$  and Then Pressed in a Hot Roller at  $130^\circ\text{C}^a$

N6/N66	Nylon 6			Nylon 66		
	$T_m$ ( $^\circ\text{C}$ )	$l_c$ ( $\text{\AA}$ )	$\alpha$	$T_m$ ( $^\circ\text{C}$ )	$l_c$ ( $\text{\AA}$ )	$\alpha$
100/0	220	44	0.30	—	—	—
70/30	218	42	0.12	255	37	0.14
50/50	209	34	0.06	254	36	0.17
30/70	—	—	—	258	40	0.25
0/100	—	—	—	261	43	0.27

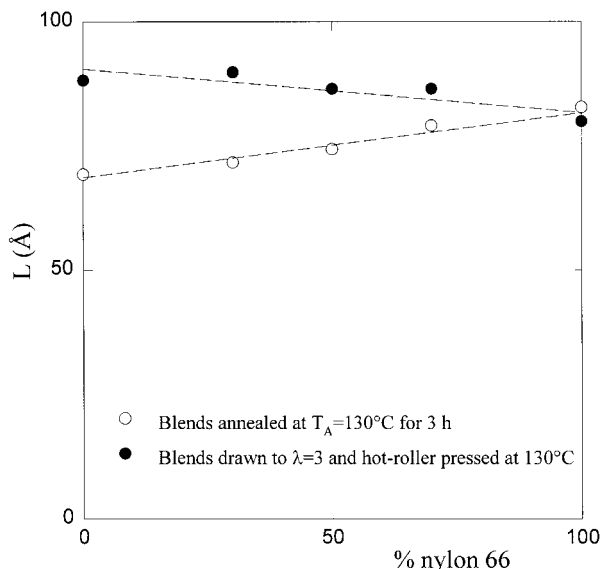
<sup>a</sup>  $T_m$ : melting temperature;  $l_c$ : thermodynamic crystal size of each individual component obtained from  $T_m$  values.

ment orientation in the drawing process to  $\lambda = 3$ . Consequently, in the filaments of intermediate composition the  $H$  increase is probably only connected to the contribution of nylon 66 component. This behavior is similar to that shown by drawn linear polyethylene (PE).<sup>26</sup> In those series of experiments, each PE sample was drawn to different  $\lambda$  values at a constant temperature, and the hardness  $H$  was measured after each deformation step. In that material,  $H_\perp$  and specially  $H_\parallel$  greatly increased as a function of draw ratio  $\lambda$ , being independent of the temperature of deformation. It is important to say that we have not found any information about the hardness dependence on  $\lambda$  in other polymeric materials drawn and measured in the same way.

Figure 9 shows the long spacings  $L$  evolution as a function of composition in the drawn and pressed series. It can be seen that  $L$  increases above the values found in the blends annealed at  $130^\circ\text{C}$  for 3 h, but the increase is inversely proportional to the nylon 66 content, i.e., it goes from 69 to 88  $\text{\AA}$  for the nylon 6 sample, and does not change for the nylon 66 one.

## CONCLUSIONS

1. Filaments of the homopolymers nylon 6 and nylon 66 when annealed at different temperatures  $T_A$  for 3 h show the same increase of the hardness as a function of  $T_A$ , the increase following an Arrhenius-type equation. This behavior could be explained by the combined effect of the higher crystallin-



**Figure 9** Dependence of long spacing  $L$  with composition in blends of nylon 6 and nylon 66. (Symbols: as in Figs. 7 and 8.)

ity of nylon 6 and possibly the higher crystalline hardness  $H_c$  values of nylon 66, thus giving rise to similar  $H$  values.

- In the filaments of blends of both types of nylon with different compositions, each component depresses the crystallization capability of the other. This influence is responsible for the hardness behavior of the samples in all range of compositions. Annealing of the blends at  $T_A = 130^\circ\text{C}$  neither modifies their crystallinity nor their mechanical properties.
- If the filaments made of blends of nylon 6 and nylon 66 are drawn to  $\lambda = 3$  and then pressed in a hot roller at  $130^\circ\text{C}$ , the crystallinity of the blends is slightly improved, and the hardness  $H$  increases with the nylon 66 content.  $H$  does not change for the nylon 6 sample. This behavior can be explained by the increase of crystalline hardness  $H_c$  in nylon 66 due to the orientation effect originated during the drawing process.

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