Annealing of isotropic nylon-6,6

Babaniyi Babatope† and David H. Isaac*
Department of Materials Engineering, University College of Swansea, Singleton Park, Swansea SA2 8PP, UK
(Received 21 December 1990; revised 13 May 1991; accepted 6 June 1991)

The effects of annealing on the mechanical properties of nylon-6,6 have been studied. Extruded, isotropic samples were annealed at temperatures in the range 60°C to 200°C for times up to 3 h (10800 s). It was found that significant increases in tensile modulus and small increases in strength were induced by annealing. The optimum annealing temperature was around 150°C, but annealing at 60°C appeared to produce more rapid improvements than at 100°C. Annealing at 200°C led to deterioration in mechanical properties. Specimens constrained to constant length during annealing were found to have less pronounced increases in modulus than unconstrained samples. These results are discussed in terms of possible microstructural changes.

(Keywords: annealing; nylon; mechanical properties)

INTRODUCTION

Nylons are polymers that have recurring amide groups as an integral part of the main chain. The most prominent of the polyamides is poly(hexa methylene adipamide), i.e. nylon-6,6, a semicrystalline high melting point thermoplastic, synthesized by Carothers in the 1930s (ref. 1). It has attained considerable commercial importance particularly in fibre form in the textile industry, and it is used increasingly as the matrix material in fibre reinforced composites.

Nylon-6,6 has been studied widely and some of the properties and behaviour have been well documented[1–3]. It has a high melting temperature (T_m) of 265°C compared with 135°C for polyethylene, and this large difference has been attributed to forces between the polar groups in the molecules. Interchain hydrogen bonds between the C=O groups of one molecule and the N–H groups of the adjacent chain have been demonstrated[2]. The glass transition temperature (T_g) of 65°C is similar to the heat distortion temperature[4]. Another important transition temperature at about 150°C–160°C in nylon-6,6 has been described by Takaganagi as the alpha crystallization temperature ($T_{\alpha c}$) (ref. 5). This is thought to correspond to a secondary transition of the polymer in which crystal subunits are capable of being moved within the larger crystal units[6].

Nylons generally have a high affinity for water, and their physical and mechanical properties are often significantly affected by the absorption of moisture. Nylon-6,6 has the highest water absorption of all the polyamides[7]. The hydrogen bonded chains and links in the disordered region that form a crosslinked network are broken easily by a number of different environmental effects such as moisture absorption, high temperature, stress and even (slowly) thermal fluctuation at room temperature[8]. Some relevant properties of nylon-6,6, such as water absorption, tensile modulus, tensile strength and maximum elongation, are typically in the region of 2%, 3 GPa, 80 MPa and 10%, respectively, for a dry specimen. An increase in the relative humidity and hence water content changes these figures significantly. For example, at a relative humidity (RH) of 65%, the tensile modulus is reduced to approximately 1.2 GPa, and when the sample is saturated with water this reduces further to 0.65 GPa (ref. 7).

Thermomechanical history, such as annealing, influences the ability of materials to undergo plastic deformation. Annealing effects on a number of polymers, for example poly(ethylene terephthalate) (PET)[5,9], polyethylene[10,11], polypropylene[12], nylon-6[8,13], nylon-6,6[5,8,13,14], have been reported. As an activation process, annealing decreases the enthalpy[15] and tends to make a polymer stiffer and more brittle. At the microstructural level, an irreversible reorganization occurs often leading to shrinkage, as illustrated for polyethylene by Pope and Keller[11]. Thus annealing is used to modify the supermolecular organization of crystalline polymers.

In an oriented polymer specimen, annealing may lead to a change in the structure of the amorphous region[12] and increase the extent of crystallization[15]. Unconstrained annealing often results in substantial changes in mechanical properties[9], while constraining a sample to a constant length during annealing has been shown to generate significant stresses and often affects the extent of property modification[14].

The annealing temperature also has a strong influence on the mechanical properties of a polymer, particularly near the transition temperatures. The changes in mechanical properties of semicrystalline polymers depend on the proportions of amorphous and crystalline phases present. More significantly, polymers are very temperature-sensitive, so that testing at elevated temperatures decreases tenacity and modulus, and increases breaking and yield strain[8]. The changes taking place in the amorphous region of the polymer have been identified to be responsible for this behaviour[16].

---

*To whom correspondence should be addressed
†Permanent address: Department of Physics, Division of Engineering Physics, Obafemi Awolowo University, Ile-Ife, Nigeria

0032-3861/92/081664–05

Despite the wealth of information available on the nylons, there still remain many areas to be explored, especially in the thermomechanical and related characteristics of isotropic samples rather than oriented fibres. Although nylons are often used in oriented fibre form, the understanding of the initial properties prior to induction of molecular orientation is necessary for a better understanding of the structure–property behaviour of the isotropic material. Furthermore, fibre-reinforced nylon composites, which are now commonly used in advanced engineering applications, normally have little or no intrinsic preferred orientation of the matrix[17].

This paper highlights the observed patterns of behaviour of initially unoriented nylon-6,6. The changes in the room temperature properties such as yield stress, yield strain and tensile modulus have been related to annealing temperature and time. The effect of water content and test temperature on tensile properties have also been considered. These results form part of some studies carried out recently on the thermomechanical behaviour and structure–property relationships of nylon-6,6 and its short fibre-reinforced composites[17].

EXPERIMENTAL

The material used in this investigation was the commercially available 'A100 Maranyl' nylon-6,6, supplied in pellet form. The product information data sheets[4] quoted a density of 1.14 g cm^{-3}, water absorption of 1.5%, tensile strength of 81 MPa at 23°C, tensile elongation of 10%, heat distortion temperature of 66°C, glass transition temperature (T_g) of 67°C, and a melting temperature of 265°C. Although tensile modulus was not quoted by the supplier[4], a value of 3.1 GPa has been determined from data reported by Ogorkiewicz[7].

The pellets were dried at 90°C for 4 h prior to extrusion through a small vertical extruding device built in this laboratory. The mould was preheated to 285°C, slightly above the required processing temperature of about 275°C, before the pellets were poured into the mould. After the mould had equilibriated to 275°C, it was held at this temperature for 10 min before extrusion commenced. Direct extrusion was carried out by allowing the nylon to come out of the orifice freely, using a 1.0 mm die diameter. The extruded fibre diameter ranged between 0.35 mm and 0.5 mm, and sections with uniform diameters in the region of 0.4 mm were used for all the tests reported.

Unconstrained annealing treatment was carried out in a conventional muffle furnace maintained at the required temperature. Fibres were annealed at temperatures of 60°C, 100°C, 150°C and 200°C for times ranging from 1800 s to 10 800 s. Specimens for mechanical testing were cut from the annealed fibres. The constrained annealing treatment was carried out by maintaining a constant specimen length between two fixed grips in an elevated temperature chamber similar to those described by Ives *et al.*[18] and used by Peiffer[5]. Fixed length specimens were placed in the chamber and then heated to the required annealing temperature, which was maintained for 1800 s before cooling to room temperature.

The annealing temperature in the muffle furnace was measured with a thermocouple that was inserted into the centre of the furnace from the top, and which was connected to external electronic devices for reading and maintaining steady temperatures. For elevated temperature testing the same thermocouple was inserted through a small hole in the glass tube of the chamber, and placed immediately adjacent to the specimen. The constant temperature hot zone was confirmed to be greater than the sample length and all temperature measurements were accurate to ±3°C.

Specimens were cut from the long lengths of annealed fibre for all mechanical measurements, and at least three samples were tested for each condition. Uniaxial tensile tests were carried out on a standard tensile testing machine (Instron 1162) in accordance with ASTM D638 at temperatures from ambient (25°C) to 200°C. All tests were performed at the cross head speed of 5 mm min^{-1}, resulting in a strain rate of about 0.2 min^{-1}. Tensile modulus was estimated by converting the force–elongation curves into stress–strain curves. The stress was estimated as force per unit cross-sectional area of the untested specimen, and strain as the elongation per unit original length. From the stress–strain curves, the yield stress and yield strain were obtained in the manner commonly used for polymers[19]. The maximum force before uniform deformation was used for the computation of the yield stress. The tensile modulus, yield stress and yield strain values were obtained and correlated with the annealing temperatures and annealing times. The measured humidity throughout the test period was 55 ± 5% RH and room temperature was between 23°C and 26°C.

A few tests were carried out to study the effects of relative humidity (water content) on the samples and to confirm that the extruded samples and measurement techniques gave results compatible with the manufacturers' figures and the literature. Specimens were prepared from fibres annealed at 60°C for one week and from others soaked in distilled water for the same period of time to obtain samples in 'dry' and 'wet' conditions, respectively. The 'dry' fibres were kept in a desiccator until required for testing.

RESULTS AND DISCUSSION

Starting material

Flat plate wide angle X-ray diffraction patterns were obtained for unannealed and annealed samples of extruded nylon-6,6, and these consisted of continuous rings, characteristic of unoriented polymers. As expected, the patterns for unannealed specimens appeared more diffuse than those of annealed specimens, although quantitative measures of crystallinity were not determined.

Figure 1 shows some typical stress–strain curves obtained from extruded but unannealed samples with different water contents. For specimens in the 'wet' condition (curve 3) the average tensile strength was ~37 MPa, with a tensile modulus ~0.54 GPa. This compared with a tensile strength of ~80 MPa, and tensile modulus ~2.81 GPa in the 'dry' condition (curve 1). However, at the ambient conditions under which the rest of this investigation was carried out (i.e. relative humidity of 55 ± 5%), the tensile strength and tensile modulus were found to be ~63 MPa and ~1.21 GPa respectively (curve 2). These experimental figures are similar to the approximate values for the tensile modulus derived from Ogorkiewicz[7] of 3.1 GPa (dry), 1.18 GPa (65% RH) and 0.65 GPa (wet).

It is well known that when designing with nylon-6,6,

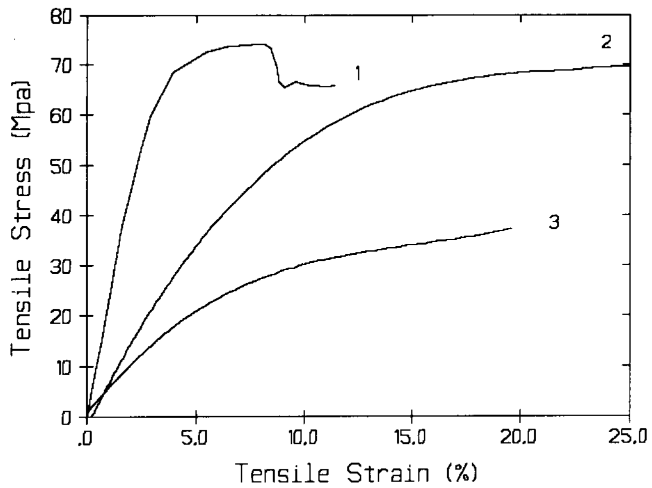

Figure 1 Stress-strain behaviour of nylon-6,6 fibre at different humidity conditions showing the effect of moisture absorption: (1) dry; (2) 55% RH; (3) 100% RH, i.e. wet

consideration of the environmental conditions is very important, due to the high affinity for water. It was found that at the ambient test conditions for this investigation (23°C-26°C and $55 \pm 5\%$ relative humidity) the mechanical properties were similar to those obtained on dry samples at 40°C-50°C (ref. 1). Thus the effect of absorbed water molecules was roughly equivalent to a 20°C rise in temperature. The tensile properties of the unannealed, 'dry' and 'wet' samples as presented in *Figure 1* are consistent with previously published work[4,7,19,20]. The values obtained at extreme humidity conditions (i.e. 0% and 100%) revealed the substantial effects of absorbed water molecules on the mechanical properties of nylon-6,6. It is thought that water molecules enter mainly the amorphous regions of the polymer, facilitating molecular motion by reducing the electrostatic forces between the molecular chains (i.e. the hydrogen bonds)[3]. This has been shown to lower the temperature of the alpha relaxation, and has been used to support the view that the alpha relaxation may be related to the glass transition temperature.

Annealing behaviour

Figure 2 shows the effect of annealing time on room temperature tensile modulus of nylon-6,6 for four different annealing temperatures. At annealing temperatures up to 150°C, the tensile modulus increases with annealing times up to about 5500 s, and there are only small changes at longer times. However, when annealing at 200°C, the tensile modulus reaches a maximum after about 3500 s and then decreases at longer times so that after 10 800 s the tensile modulus is only 0.86 GPa (well below the unannealed value of 1.21 GPa). Although the largest modulus increase occurs following annealing at 150°C, it is interesting to note that annealing at 60°C appears to produce more rapid improvement than at 100°C.

Figure 3 shows the effect of annealing time on yield stress for the four different annealing temperatures. At annealing temperatures up to 150°C, there appears to be a small but steady increase in yield stress with annealing time although the changes are not as significant as those observed for tensile modulus (*Figure 2*). At 200°C, however, the yield stress decreases steadily from a value in the unannealed state of about 63 MPa to 35 MPa after annealing for 10 800 s. It should be noted that, as for the tensile modulus changes, the yield stress is improved most significantly following annealing at 150°C, and that greater increases are observed at 60°C than at 100°C.

The variation in mechanical properties resulting from annealing over the temperature range 60°C-150°C can be rationalized in terms of the microstructural changes. The two important mechanisms are thought to be rupture of hydrogen bonds and chain mobility or relaxation. At 60°C (just below T_g) hydrogen bond rupture may occur, but chain motion is restricted so that load bearing molecules such as taut-tie segments retain their mechanical capability. At 100°C, in addition to hydrogen bond rupture, chain segment motion or relaxation in the amorphous areas is possible so that more significant chain rearrangement can occur. It is thought that at this temperature some relaxation in the load bearing chains will lead to poorer overall mechanical performance compared with samples annealed just below T_g. At 150°C, the optimum crystallization temperature, substantial chain motion may occur, leading to increased crystallinity

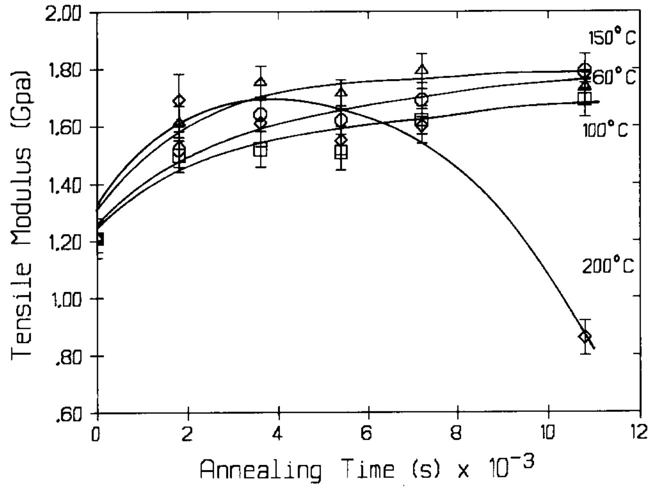

Figure 2 Tensile modulus against annealing time at four different annealing temperatures: (○) 60°C; (□) 100°C; (△) 150°C; (◇) 200°C

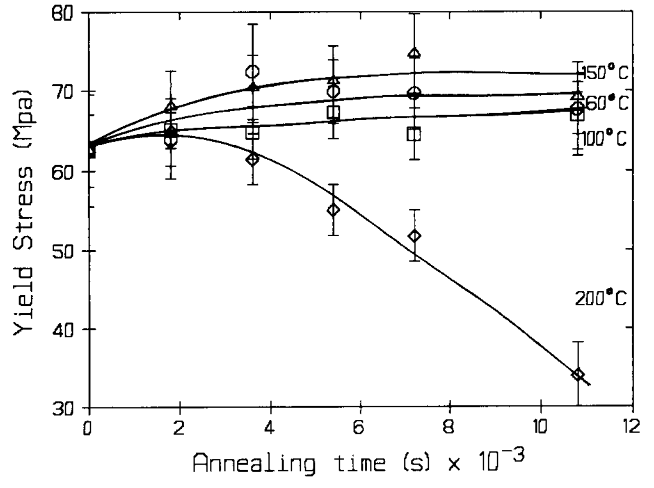

Figure 3 Yield stress against annealing time at four different annealing temperatures: (○) 60°C; (□) 100°C; (△) 150°C; (◇) 200°C

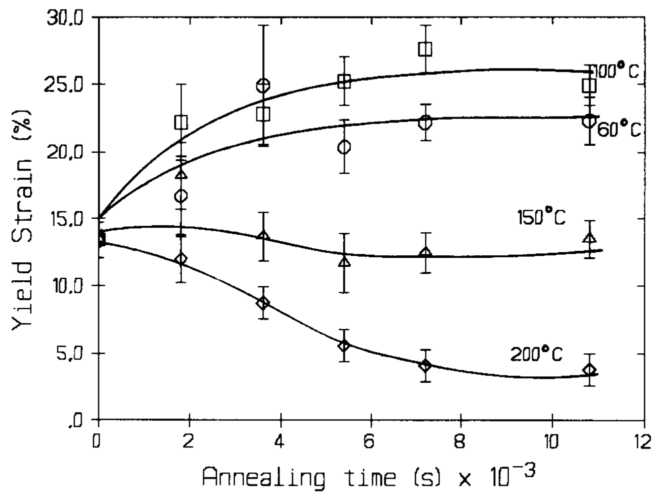

Figure 4 Yield strain against annealing time at four different annealing temperatures: (○) 60°C; (□) 100°C; (△) 150°C; (◇) 200°C

and hence more significant improvements in modulus and strength.

Annealing at temperatures up to 150°C gave rise to no deterioration in properties, irrespective of annealing time. However, at 200°C and longer annealing times, the taut-tie molecules, which support most of the applied stress, are subjected to thermal degradation, resulting in a sharp deterioration in tensile properties.

Figure 4 shows how the room temperature yield strain varies with annealing time for a range of annealing temperatures. With an annealing temperature of 60°C, yield strain increases from the unannealed value of about 13%, to ~21% at the annealing time of 6000 s and remains almost constant at longer times. For an annealing temperature of 100°C, yield strain increases to a value of about 25% for annealing times above 6000 s. Following annealing at 150°C, yield strain appears not to vary significantly from the value of 13% obtained for an unannealed specimen. Annealing at 200°C causes the yield strain to decrease steadily from the unannealed value of 13% to about 3.5% for long annealing times.

It has already been shown (*Figure 2*) that when nylon fibres are allowed to contract freely during annealing, increases in tensile modulus are induced. *Figure 5* (unconstrained, curve 1) shows the extent of these increases as a function of annealing temperature for an annealing time of 1800 s. However, when samples are constrained to a constant length during annealing, the resulting mechanical behaviour is quite different. Decreases in tensile modulus are observed. In the case of unconstrained heating, the tensile modulus is increased by annealing but does not vary significantly with annealing temperature. In contrast, with constrained annealing a minimum in tensile modulus is seen for annealing temperatures of about 60°C to 80°C, followed by a maximum for an annealing temperature of 150°C.

Similar behaviour has been reported in the past by Statton in his work on the thermomechanical studies of nylon-6,6 fibres[9]. Unconstrained annealing treatment of oriented polymer fibres causes a refolding of the extended chains, producing a larger amount of refolding than in constrained annealing[9]. The observed increases in tensile modulus (within the annealing time range of this investigation) at annealing temperatures below 160°C may be due to the combined effects of chain packing, as a result of rapid crystallization, and reduced randomization in the amorphous phase.

Effects of annealing on high temperature properties

Figures 6 and *7* show the tensile modulus and yield stress of annealed nylon-6,6 fibres at elevated temperatures. It has already been shown (*Figures 2* and *3*) that room temperature tensile modulus and yield stress are dependent on annealing temperature and time. However, at elevated test temperatures, these tensile properties appear to be relatively independent of the prior annealing conditions.

It has been reported previously[21] that at temperatures close to $(T_g + T_m)/2$, which is about 150°C for nylon-6,6, a maximum crystallization rate occurs. This temperature therefore defines an important annealing range in which a rapid induction of crystallization equilibrium can be achieved. Thus it is at this annealing temperature that chain packing and reduced randomization in the amorphous phase are optimized. Above this temperature a non-uniform weakening due to thermal fluctuation and chain degradation occurs. It is interesting to note that

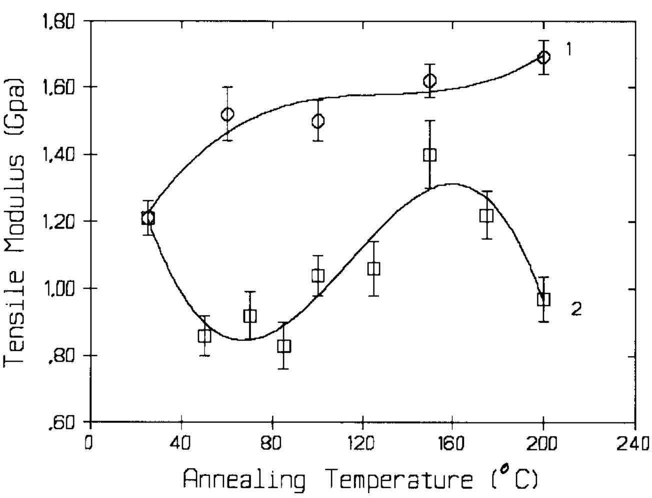

Figure 5 Tensile modulus against annealing temperature following: (1) unconstrained; (2) constrained annealing for 1800 s

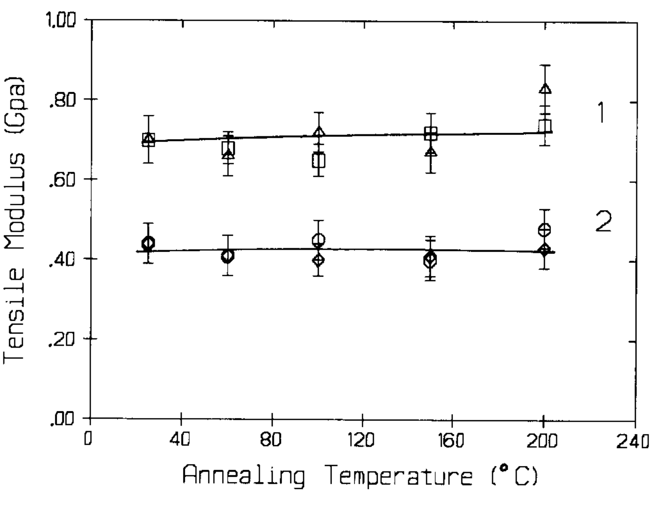

Figure 6 Tensile modulus against annealing temperature for elevated test temperatures: (1) modulus at 60°C for annealing times of 1800 s (□) and 10800 s (△); (2) modulus at 150°C for annealing times of 1800 s (○) and 10800 s (◇)

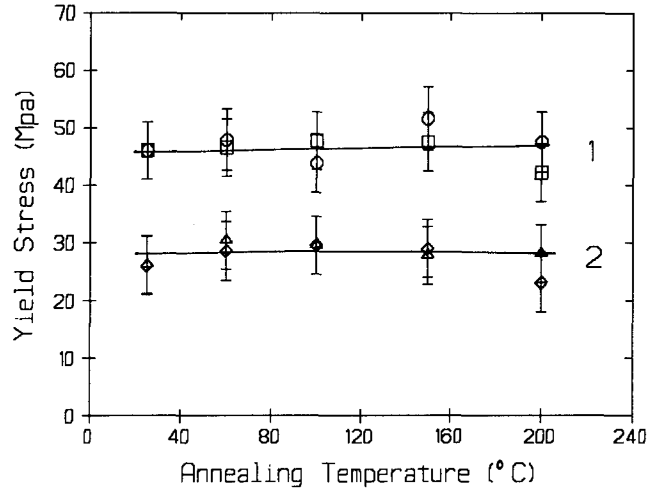

Figure 7 Yield stress against annealing temperature for elevated test temperatures: (1) yield stress at 60°C for annealing times at 1800 s (○) and 10 800 s (□); (2) yield stress at 150°C for annealing times of 1800 s (△) and 10 800 s (◇)

the temperature range of 100°C–200°C has been identified in the past as the Brill transition range[22,23] at which property changes take place in nylon-6,6. This Brill transition has been reported to affect the yield behaviour of nylon-6,6 at 160°C, and the effect has been attributed to a reversible crystal–crystal phase transition[19].

CONCLUSION

It has been shown that the room temperature tensile properties of isotropic extruded nylon-6,6 depend on the annealing conditions. At annealing temperatures up to 150°C the tensile modulus, and to a lesser extent the yield stress, increase with annealing time. At an annealing temperature of 200°C, however, both modulus and strength are affected adversely. Although annealing at 150°C has been found to produce greatest improvement in performance, more significant changes are induced at 60°C than at 100°C.

The microstructural mechanisms that occur at 60°C, 100°C and 150°C, which determine mechanical properties, are thought to be chain rearrangement due to hydrogen bond rupture, relaxation of the load bearing taut-tie molecules and more significantly chain motion leading to increased crystallinity. At 200°C, chain degradation is the likely cause of the reduction in mechanical properties.

The mechanical tests carried out at elevated temperatures (i.e. 60°C and 150°C) gave results almost independent of the prior annealing conditions. More significant improvements were achieved during unconstrained annealing than when the sample was constrained. Constrained annealing at lower temperatures produced a decrease in modulus and the optimum annealing temperature was found to be 150°C.

ACKNOWLEDGEMENTS

We would like to thank the Obafemi Awolowo University, Ile-Ife, Nigeria for providing funding to B.B., and Paul Shipton of Courtaulds Research for constructive discussions and provision of materials.

REFERENCES

1 Kohan, M. I. (Ed.), 'Nylon Plastics', John Wiley Interscience, New York, 1973
2 Perkin, W. G. and Porter, R. S. *J. Mater. Sci.* 1977, **12**, 2355
3 McCrum, N. G., Read, B. E. and Williams, G., 'Anelastic and Dielectric Effects in Polymeric Solids', John Wiley and Sons, New York, 1967
4 Courtaulds Technical and product information data sheets 1987
5 Peiffer, D. G. *Polym. Eng. Sci.* 1981, **21**, 449
6 Aharoni, S. M. *Polym. Eng. Sci.* 1979, **19**, 450
7 Ogorkiewicz, R. M. (Ed.), 'Engineering Properties of Thermoplastics', John Wiley Intersience, New York, 1970
8 Hearle, J. W. S. and Vaughan, E. A. 'Polymer Science', (Ed. A. D. Jenkins), North Holland Publ. Co., Vol. 1, 1972, p. 823
9 Statton, W. O. *J. Polym. Sci. Polym. Symp.* 1971, **32**, 219
10 Clement, J., Jakeway, R. and Ward, I. M. *Polymer* 1979, **20**, 295
11 Pope, D. P. and Keller, A. *J. Mater. Sci.* 1977, **12**, 1105
12 Yefimov, A. V., Lapshin, V. P., Fartunin, V. I., Vozlov, V. P. and Bakeyev, N. F. *Polym. Sci. USSR, Vysokomol Soyed.* 1983, **A25**, 692
13 Shimada, T. and Porter, R. S. *Polymer* 1981, **22**, 43
14 Elad, J. and Schultz, J. M. *J. Polym. Sci. Polym. Phys. Edn.* 1984, **22**, 781
15 Matsuoka, S. *Polym. Eng. Sci.* 1974, **14**, 162
16 Frenkel, S. *J. Polym. Sci. Polym. Symp.* 1977, **58**, 185
17 Babatope, B. *PhD Thesis* University of Wales, 1989
18 Ives, G. C., Mead, J. A. and Riley, M. M. 'Handbook of Plastic Tests Methods', ILIFFE Books (London), 1971
19 Hartman, B. and Cole, R. F. *Polym. Eng. Sci.* 1985, **25**, 65
20 Prevosek, S., Kwon, Y. D. and Sharma, R. H. *J. Mater. Sci.* 1977, **12**, 2310
21 Brydson, J. A., 'Polymer Science' (Ed. A. D. Jenkins), North Holland Publ. Co., Vol. 1, p. 193
22 Starkweather, H. W., Zoller, P. and Jones, G. A. *J. Polym. Sci. Polym. Phys. Ed.* 1981, **19**, 467
23 Itoh, T. *Japn J. Appl. Phys.* 1976, **15**, 2295