

# Effect of Prior High-Pressure Treatment on Nylon 6 Films: Swelling and Other Studies

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## Synopsis

The effect of prior high-pressure treatment on nylon 6 films has been investigated, using weight swelling, density, infrared crystallinity index, x-ray diffraction, and relative viscosity measurements. Pressures in the range of 0–25 tons/sq. in. were used. Swelling measurements, using benzyl alcohol as the swelling agent, show that the initial slope of the weight swelling-versus-(time)<sup>1/2</sup> plots, divided by equilibrium weight swelling, increases with increasing pressure, indicating enhancement of the diffusion coefficient with pressure. The sigmoidal nature of the plots is reduced with pressure, but the relaxation-controlled non-Fickian behavior persists within the pressure range used. With increase of pressure up to 10 tons/sq. in., the equilibrium weight swelling records a substantial increase, and slight increases in density and infrared crystallinity are concomitantly observed but an opposite effect occurs with x-ray order factor. Beyond 10 tons/sq. in. pressure, these quantities become more or less stationary. Relative viscosity of formic acid solution of pressure-treated samples remains unaltered with pressure. An integrated interpretation of all these changes is found in the degeneration of larger crystallites into smaller ones with the molecules sandwiched between new surfaces. The newly created crystallites are too small to produce x-ray diffraction peaks. Pressure-induced  $\gamma \rightleftharpoons \alpha$  conversion processes are also found to occur.

## INTRODUCTION

Textile fibers and films in commercial use are subjected to a variety of stresses during processing and in subsequent use. The resulting deformations, which are not simple and last for various periods, play a predominant role in the behavior of polymeric materials of textile and other industrial interest. In a warp beam, large compressive radial pressures are developed at the yarn-barrel interface due to the warping procedures. Time and temperature dependence of thermomechanical properties of oriented polymeric yarns may lead to increase in barrel pressures. Laboratory experiments with certain nylon yarns<sup>1</sup> have shown an increase in barrel pressure from 0.7 ton/sq. in. at 70°F to as high as six times this amount, for a wind thickness of only 6 in., due to prolonged storage at 130°F. Moreover, the barrel pressures would increase with increasing wind thickness.

Very little seems to have been reported regarding the effect of large compressive stress on polymer morphology and structure and on the swelling and dyeing properties of textile materials. Recently, an electron-microscopic study<sup>2</sup> of nylon 66 films previously subjected to elevated compressive pressures has shown degeneration of spherulite ribbons into fibrils due to pressure of 25 tons/sq. in.

The present work is concerned with the study of the effects of compressive pressures on nylon 6 films, using weight swelling and other methods. Solvent uptake has been used before<sup>3</sup> as an efficient tool for structural investigations of

polymers. Benzyl alcohol has been used as the swelling agent at 23°C because it has been found to have remarkable swelling action on nylon 6.<sup>5</sup> The other methods used for this investigation involve density, viscosity, x-ray order factor, and infrared crystallinity index determinations. The experiments were not done at elevated pressures *in situ*, but the films were subjected to high-pressure treatment before the experiments. No appreciable relaxation of pressure effects was observed during a fortnight. Thus, because of the very long relaxation times, virtually no relaxation of pressure effects occurs during the small time gap between pressure treatment and experiment.

## EXPERIMENTAL

### Materials

**Nylon 6 Film.** Unstretched nylon 6 films used in the present work were obtained from the Garware Synthetics, India, in 40–50 $\mu$  thickness. The films were produced by extrusion at about 2–3 atm pressure followed by rapid quenching. These films showed highly spherulitic structure. Both the  $\alpha$  and  $\gamma$  crystalline phases were present in the films. The total x-ray order factor was found to be 0.28 in the films which had a density of 1.135 g/cm<sup>3</sup>. Before use for sample preparation, nylon 6 films were cleaned with acetone for removing surface impurities and then dried in an electrical oven at 105  $\pm$  1°C to constant weight. The dried films were preserved in a vacuum desiccator over phosphorus pentoxide for at least 48 hr before use.

**Chemicals.** Benzyl alcohol and acetone used for surface cleaning were obtained from the BDH in analar grade and were used without further purification.

### Samples

Pressed samples of nylon 6 for swelling and other studies were prepared by cutting from nylon 6 films discs of precisely the same size as the die of a hand-operated hydraulic press, supplied by the Research and Industrial Co., England. The nylon 6 discs fitted into the die exactly, leaving no annular space between their circumference and the die wall so that no expansion of the discs could occur during the application of pressure. Pressed samples were prepared by putting five discs in the die at a time or putting them in one at a time. The discs were subjected to different pressures, viz., 5, 10, 15, 20, and 25 tons/sq. in., for 30 min. These samples were preserved in a vacuum desiccator over phosphorus pentoxide for more than 48 hr to remove moisture completely and were then used for swelling, density, viscosity, x-ray diffraction, and infrared studies.

### Swelling Experiments

The swelling measurements made in the present work refer to weight swelling at 23°C. Pressed samples dried over phosphorus pentoxide were taken for weight swelling measurements in benzyl alcohol. The degree of swelling,  $\alpha$ , was calculated in percentage weight swelling by using the following equation:

$$\alpha = \frac{W_1 - W_0}{W_0} \times 100$$

where  $W_0$  = weight of the unswollen sample and  $W_1$  = weight of the swollen sample.

The weight of a swollen sample was determined after removing the sample from the solvent and sandwiching it between filter paper to soak away the surface solvent completely. The kinetics of swelling was determined on the same samples by immersing them in the solvent, taking them out after some recorded time, soaking off the surface solvent with filter paper, followed by weighing, and again immersing the sample for some recorded time and repeating the same procedure several times until equilibrium swelling was reached.

### Density

The density of the polymer films was determined by employing the flotation titration technique.<sup>4</sup> This technique consists in gradually mixing two liquids of densities above and below that of the polymer film taken. At a particular ratio of the component liquids, the density of the mixture equals that of the polymer film; and at this endpoint the polymer film neither floats on the surface nor sinks to the bottom of the mixture but floats completely immersed inside the mixture. The density of the mixture at the endpoint can be determined by separate experiment or by calculation using the volumes of the two mixed liquids and their densities at the temperature of the experiment.

The two liquids chosen for density work were carbon tetrachloride and toluene. These two liquids have no chemical action and only a negligible swelling action on nylon 6, carbon tetrachloride producing an equilibrium weight swelling of about 2% and toluene, of 0.68% in the nylon 6 films<sup>5</sup> used in the present work. The error in density measurements on this account has been calculated to appear in the fourth decimal place.

### Relative Viscosity

Nylon 6 films subjected to different prior pressure treatment as well as control films were dissolved in 85% formic acid, and the relative viscosity of the solutions was measured in an Oswald viscometer No. 1 at  $24 \pm 0.5^\circ\text{C}$ , using solutions of concentration 0.2 g/100 ml. Flow times of the solutions were measured to an accuracy of 0.2 sec. Relative viscosity  $\eta_r$  was calculated using the relation

$$\eta_r = \frac{\text{flow time of solution}}{\text{flow time of solvent}}$$

### X-Ray Diffractometry

X-Ray diffraction patterns of control nylon 6 samples as well as of those subjected to prior pressure treatment were recorded in a Philips PW 1009 x-ray diffraction unit, using Ni-filtered  $\text{CuK}_\alpha$  radiation. The x-ray order factor  $O_f$  in the films was calculated from the diffractograms, using the relation

$$O_f = 1 - \frac{m_1 + 2m_2 + \dots + m_{n-1}}{h_1 + h_2 + \dots + h_n}$$

where  $h_1, h_2, \dots, h_n$  are the heights of the diffraction peaks measured from a

suitable baseline; and  $m_1, m_2, \dots, m_{n-1}$  are the heights of the minima between the peaks. This formula has been used before<sup>6</sup> to obtain x-ray order factor.

### Infrared Crystallinity Index

It is known from the works of Miller<sup>7</sup> and Hallows and Keighley<sup>8</sup> that the  $930\text{ cm}^{-1}$  band in the infrared spectrum of nylon 6 is associated with the crystalline regions and the  $1120\text{ cm}^{-1}$  band, with the amorphous regions. In the present work, these two bands were used for calculating the infrared crystallinity index for control and pressed samples, defined as below:

$$\text{infrared crystallinity index} = \frac{\text{absorbance at } 930\text{ cm}^{-1}}{\text{absorbance at } 1120\text{ cm}^{-1}} = \frac{D_{930}}{D_{1120}}$$

The infrared spectra of the samples were recorded on a Perkin-Elmer model 21 spectrophotometer scanning in the region  $5000\text{--}650\text{ cm}^{-1}$  or a Perkin-Elmer model 457 spectrophotometer, scanning in the region  $4000\text{--}250\text{ cm}^{-1}$ .

## RESULTS AND DISCUSSION

### Weight Swelling

We investigated the kinetics of weight swelling of nylon 6 films previously subjected to different pressures in the range of 0–25 tons/sq. in. Figure 1 shows the plots of percentage weight swelling versus  $(\text{time})^{1/2}$  at  $23^\circ\text{C}$  for different pressures. These plots show a sigmoidal nature. This characteristic is also prominent in the plot for the control sample which is subjected only to atmospheric pressure. Three distinct stages in the adsorption of liquid characterized by different slopes in any of the plots in Figure 1 can be recognized. The first

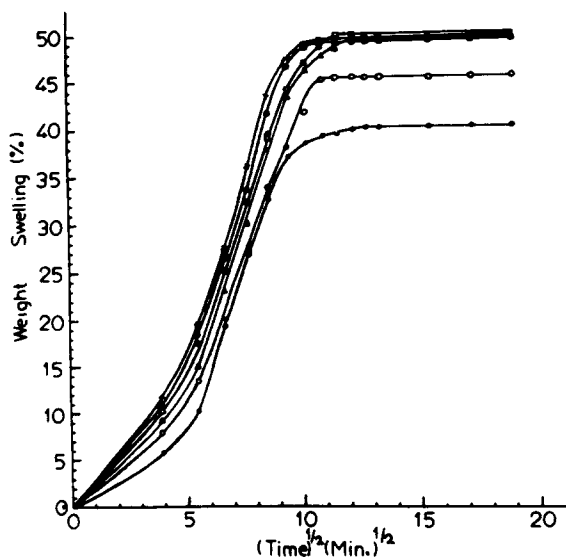


Fig. 1. Plot of percentage weight swelling at  $23^\circ\text{C}$  vs.  $(\text{time})^{1/2}$  for pressure-treated nylon 6 films: (●) atmospheric pressure; (○) 5 tons/in.<sup>2</sup>; (Δ) 10 tons/in.<sup>2</sup>; (□) 15 tons/in.<sup>2</sup>; (⊙) 20 tons/in.<sup>2</sup>; (×) 25 tons/in.<sup>2</sup>.

stage starts with the immersion of the sample in benzyl alcohol and continues for 15 to 20 min. This is followed by the second stage, characterized by a larger slope. The slope starts decreasing after a total immersion period of 64–80 min, marking the onset of the third stage. The third stage extends to the attainment of equilibrium in the weight-swelling process.

The effects of prior pressure treatment of nylon 6 films on the kinetics of weight swelling are manifested in two ways, namely, in the reduction of the sigmoidal nature of the kinetic plots and in the change of slope in the initial stage of the weight swelling. These effects are of great interest from the point of view of structural changes brought about by the prior pressure treatment and may be used as probes for these changes. As such, they merit a somewhat detailed discussion.

It is seen from Figure 1 that the sigmoidal nature of the kinetic plots has an increasing tendency to be reduced with increasing pressure. The process of solvent uptake by a polymer sample is a diffusion-controlled one. The sigmoidal nature of the kinetic plots is correlated with the nature of the process. Alfrey<sup>9</sup> has shown that a process involving a normal Fickian diffusion in a polymer film immersed in a fluid is characterized by a linear relationship between preequilibrium weight gain of the sample and the square root of time. In the case of a relaxation-controlled non-Fickian process,<sup>10</sup> the relationship with time is a linear one before equilibrium is reached. In Figure 1 the plots are not straight lines. Moreover, in Figure 2 the plots of percentage weight swelling versus time are seen to be straight lines within the limits of experimental accuracy. These facts underline the relaxation-controlled non-Fickian nature of the whole sorption process involved.

In Table I we have entered the initial slope of each plot in Figure 1 after dividing the slope by the corresponding equilibrium weight swelling. This quantity is known<sup>11</sup> to give  $D_p^{1/2}/l$ , where  $D_p$  is the diffusion coefficient of the solvent molecules through the polymer film treated at pressure  $p$  and  $l$  is the thickness of the film. We shall see later that the density of the film due to the pressure treatment increases from 1.135 g/cm<sup>3</sup> to 1.137 g/cm<sup>3</sup> as the pressure increases from 0 to 25 tons/sq. in. Since the area of the film is constrained to remain

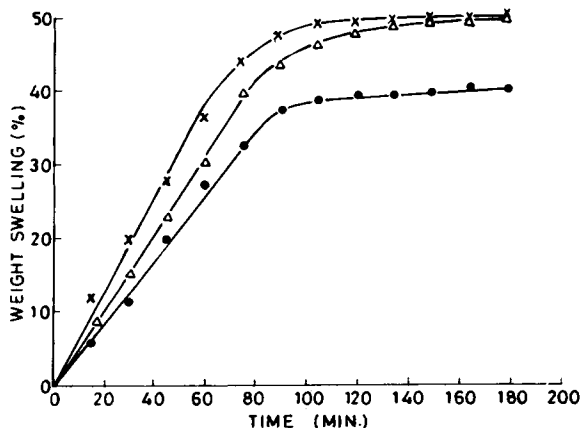


Fig. 2. Variation of percentage weight swelling at 23°C with time for pressure-treated nylon 6 films: (●) atmospheric pressure; (Δ) 10 tons/in.<sup>2</sup>; (×) 25 tons/in.<sup>2</sup>.

TABLE I  
Variation of  $D_p^{1/2}/l$  for Benzyl Alcohol in Nylon 6 Films at 23°C with Pressure

Additional pressure, tons/sq. in.	$D_p^{1/2}/l, \text{min}^{-1/2}$	$D_p/D_0$
0	0.037	1
5	0.045	1.46
10	0.048	1.69
15	0.053	2.30
20	0.056	2.31
25	0.061	2.76

constant, this means that the thickness of the film is reduced at the utmost by a factor of 0.998 due to the pressure treatment. Taking this factor as near unity, we entered in the third column of Table I the ratio  $D_p/D_0$ , where  $D_0$  is the diffusion coefficient through the control film which is not subjected to pressure treatment. We can see that this ratio varies from 1 to 2.76 as the pressure increases from 0 to 25 tons/in.<sup>2</sup> Thus, the diffusion coefficient of benzyl alcohol molecules through nylon 6 films increases initially by a factor of more than 2.5 as the pressure increases from 0 to 25 tons/in.<sup>2</sup> This effect seems to be responsible for a tendency toward reduction in the sigmoidal shape of the kinetic plots with increasing pressure, there being no appreciable increase of slope in the plots in the second stage with increasing pressure.

All these changes in the kinetics of weight swelling are indicative of structural changes in the nylon 6 films brought about by pressure. These changes may be in the form of cracks, rupture, changes of spherulite morphology, changes of order in the crystalline regions, and filling up of voids. Tensile stress is known to produce degeneration of spherulite ribbons into fibrils. Electron-microscopic evidence of degeneration of spherulite ribbons into fibrils due to prior pressure treatment exists in the case of nylon 66 films.<sup>2</sup> Moreover, x-ray diffraction study has revealed the degeneration of larger crystallites into smaller ones in this case. So far as diffusion is concerned, all these processes might be acting in opposite directions. For instance, it is known from the works of Dumbleton and Murayama<sup>12</sup> that the  $T_g$  of a semicrystalline polymer is a function of  $X/V$ , where  $X$  is the total amount of crystallinity and  $V$  is the average volume of a crystallite. Increasing crystallinity raises the  $T_g$ , and the same kind of effect is produced by decreasing the crystallite size. This implies that if the formation of smaller crystallites from larger ones occurs in nylon 6, the  $T_g$  of nylon 6 in benzyl alcohol, which occurs<sup>13</sup> around 6.5°C, should be raised and the diffusion process at 23°C would be retarded due to prior pressure treatment, which is not observed. On the other hand, formation of cracks and chain rupture due to pressure treatment may enhance the diffusion rate. If chain scission becomes a predominant effect, the reduction in molecular chain length would reduce the  $T_g$  and enhance the diffusion.

A significant effect of prior pressure treatment on the weight swelling behavior of nylon 6 films in benzyl alcohol at 23°C is found in equilibrium weight swelling. The effect is seen in Figure 3. The plot of equilibrium weight swelling versus pressure shows a remarkable increase in equilibrium weight swelling due to elevated pressures up to 10 tons/in.<sup>2</sup>, followed by stationary values. In fact, a total increase of 25% is observed in the equilibrium weight swelling. This effect can

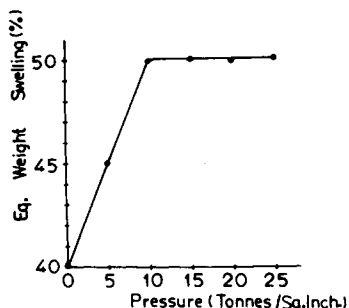


Fig. 3. Variation of equilibrium weight swelling at 23°C of pressure-treated nylon 6 films with applied pressure.

result only from the creation, due to prior pressure treatment, of more surfaces and regions in nylon 6 films in which adsorption of solvent molecules can occur. New adsorbing surfaces may come into being due to formation of cracks and degeneration of larger crystallites into smaller ones as an effect of elevated pressures. These processes would also give rise to disordered regions between new crystal surfaces containing tie molecules which would take part in the weight swelling process. Moreover, if chain scission occurs appreciably as an effect of high-pressure treatment, terminal sites for uptake of benzyl alcohol may be created and lead to greater equilibrium weight swelling. These possibilities need checking by density, crystallinity, crystal size, and viscosity measurements. The results of these measurements are discussed below.

### Density

Figure 4 is a plot of density of nylon 6 films after prior pressure treatment against pressure. The density is found to increase, though to a small extent, due to the pressure treatment up to a pressure of 10 tons/in.<sup>2</sup>. The density attains an equilibrium value after this pressure. The small increase in density observed, viz., 0.02 g/cm<sup>3</sup>, has been confirmed by density measurements on at least ten treated samples and is outside the limits of experimental error by an order of magnitude. This effect may be the result of filling up of voids, formation of more regions of crystalline order, and also conversion of the  $\gamma$  crystal form<sup>14</sup> having a density 1.163 g/cm<sup>3</sup> into the  $\alpha$  crystal form<sup>15</sup> of density 1.235 g/cm<sup>-3</sup>.

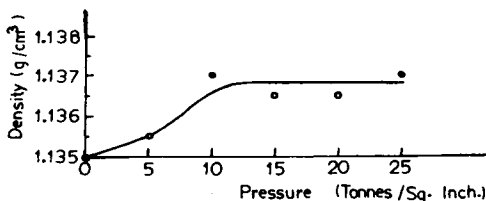


Fig. 4. Variation of density of pressure-treated nylon 6 films with applied pressure.

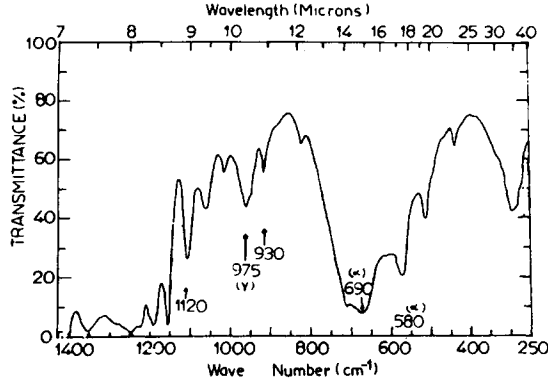


Fig. 5. Infrared spectrum of nylon 6 film not subjected to additional pressure.

### Infrared Crystallinity Index

The infrared bands at 930 and 1120  $\text{cm}^{-1}$  which have been used for calculating the infrared crystallinity index are seen in the infrared spectrum of control nylon 6 films shown in Figure 5. In Figure 6, the plot of infrared crystallinity index, as defined by  $D_{930}/D_{1120}$ , against applied pressure to which the films have been subjected reflects the same trend as exhibited by the density-versus-pressure plot in Figure 4. The trend in Figure 6 suggests that the crystallinity has slightly increased due to the pressure treatment. This increase in crystallinity might be due to the  $\gamma \rightarrow \alpha$  conversion and growth of ordered regions due to the pressure treatment.

### X-Ray Order Factor

Figure 7 is a plot of x-ray order factor in pressure-treated nylon 6 films against

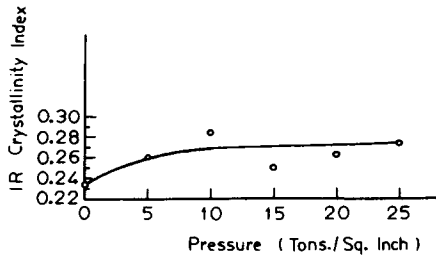


Fig. 6. Variation of infrared crystallinity index  $D_{930}/D_{1120}$  in pressure-treated nylon 6 films with applied pressure.

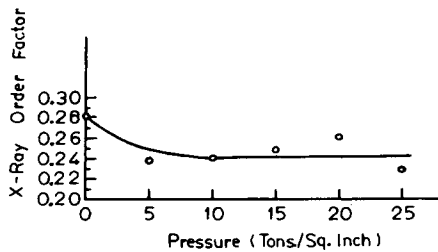


Fig. 7. Variation of x-ray order factor in pressure-treated nylon 6 films with applied pressure.



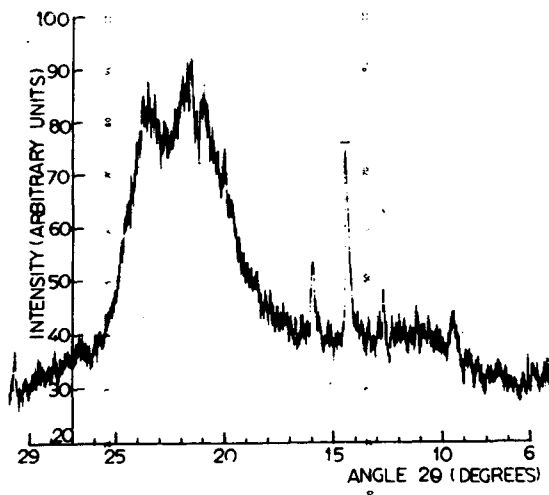


Fig. 8. X-Ray diffractogram of control nylon 6 film not subjected to additional pressure.

applied pressure. The x-ray order factor has been obtained using x-ray diffractograms of pressure-treated films for applied pressures of 0, 5, 10, 15, 20, and 25 tons/in.<sup>2</sup> It is seen that due to the pressure treatment, there occurs a slight decrease in x-ray order factor to a more or less steady value at a pressure of 10 tons/in.<sup>2</sup> and higher pressures. It is significant that the decrease in x-ray order factor occurs when the corresponding density and the infrared crystallinity index are indicating an increase in crystallinity. These contrasting trends may be the result of the requirement that in order to be able to produce x-ray diffraction peaks and to contribute to x-ray order factor, the crystallite size or the size of the ordered regions must exceed a minimum. The observed results then imply that the crystallite size has been reduced and disordered regions have come into being due to the pressure treatment. This conclusion is the same as the conclusion reached from swelling studies regarding degeneration of larger crystallites into smaller ones and creation of disordered regions. The effect has occurred to such an extent that the minimum size requirement for x-ray diffraction is not satisfied.

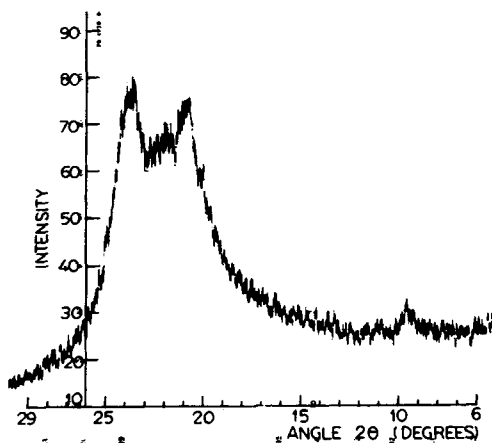


Fig. 9. X-Ray diffractogram of pressure-treated nylon 6 film. Pressure: 5 tons/in.<sup>2</sup>

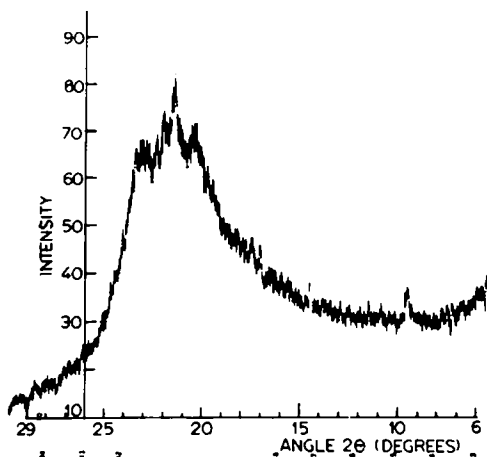


Fig. 10. X-Ray diffractogram of pressure-treated nylon 6 film. Pressure: 15 tons/in.<sup>2</sup>

Figures 8 through 11 show the x-ray diffractograms of nylon 6 films subjected to 0, 5, 15, and 25 tons/sq. in. pressures, respectively. We have not tried to obtain quantitative information about the effect of elevated pressure on the crystallite size from these diffractograms because the intensity half-width of the diffraction peaks cannot be meaningfully determined with dependable accuracy due to considerable overlap. But a small broadening of the diffraction peaks with

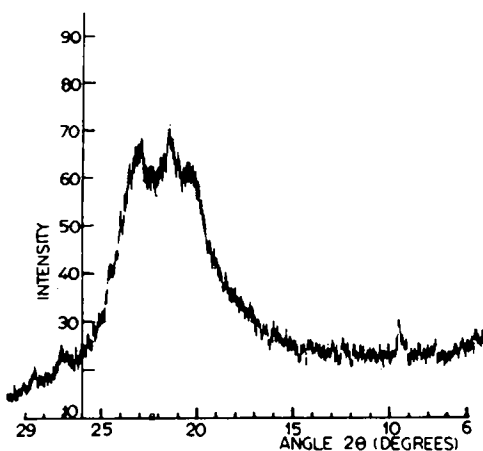


Fig. 11. X-Ray diffractogram of pressure-treated nylon 6 film. Pressure: 25 tons/in.<sup>2</sup>

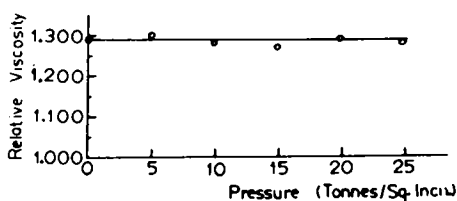


Fig. 12. Plot of relative viscosity of formic acid solution of pressure-treated nylon 6 films vs. pressure.

pressure, indicating reduction in crystallite size, is apparent from these diffractograms. Apart from this effect, it is seen that prior pressure treatment causes an exchange of intensity between the diffraction peak at  $2\theta = 21^\circ 25'$ , which is due to the  $\gamma$  crystal form,<sup>16</sup> and those at  $2\theta = 20^\circ 7'$  and  $23^\circ 55'$ , which are due to the  $\alpha$  crystal form,<sup>16</sup> which indicates a pressure-induced  $\gamma \rightleftharpoons \alpha$  conversion. In fact, a  $\gamma \rightarrow \alpha$  conversion process is seen to occur distinctly at a pressure of 5 tons/in.<sup>2</sup> while at higher pressures a  $\gamma \leftarrow \alpha$  conversion process sets in, which loses predominance to the  $\gamma \rightarrow \alpha$  conversion process again at 25 tons/in.<sup>2</sup> pressure. Thus, pressure treatment causes a kind of instability in the equilibrium between the crystal forms, which depends upon the pressure applied.

### Relative Viscosity

In order to ascertain if pressure treatment brings about any mechanical degradation in the form of change in molecular chain lengths by causing scission, we have determined the relative viscosity of formic acid solutions of pressure-treated nylon 6 samples. In Figure 12 we see that the plot of relative viscosity versus pressure for pressure-treated samples is a straight line parallel to the pressure axis in the pressure range used. This leads to the conclusion that no reduction in molecular chain lengths occurs at elevated pressures. Therefore, the acceleration in the initial swelling kinetics and in the diffusion process in pressure-treated nylon 6 films immersed in benzyl alcohol cannot be attributed to chain scission.

### CONCLUSIONS

In conclusion, it may be said that substantial structural information about nylon 6 films subjected to prior pressure treatment has been obtained from swelling studies and studies of density, crystallinity, x-ray diffraction patterns of pressure-treated samples, and of relative viscosity of their formic acid solutions. One of the most significant effects of pressure treatment brought out by these studies is the degeneration of larger crystallites into smaller ones, with tie molecules appearing in the disordered regions between the newly created surfaces. A tendency toward creation of crystalline order over very small regions, mostly not meeting the minimum size requirement for producing x-ray diffraction, is indicated by a slight increase in density and infrared crystallinity index. Studies of x-ray diffraction patterns of pressure-treated nylon 6 films show that pressure-induced  $\gamma \rightleftharpoons \alpha$  conversion processes occur with alternating predominance of one or the other of the two processes depending upon pressure applied.

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### References

1. S. K. Batra, D. S. Lee, and S. Backer, *Text. Res. J.*, **46**, 453 (1976).
2. N. K. Chaudhuri and N. V. Bhat, *Nucl. Phys. Solid State Phys.*, **18C**, 301 (1975).
3. D. A. Blackadder and P. I. Vincent, *Polymer*, **15**, 2 (1974).
4. W. R. Moore and R. P. Sheldon, *Polymer*, **2**, 315 (1961).
5. L. P. Singh, M.Sc. (Tech.) Thesis, University of Bombay, 1977.
6. B. R. Manjunath, A. Venkatraman, and T. Stephen, *J. Appl. Polym. Sci.*, **17**, 1091 (1973).
7. R. L. Miller, in *Encyclopedia of Polymer Science and Technology*, Vol. 4, H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds., Wiley-Interscience, New York, 1966, p. 449.
8. R. S. Hallows and J. H. Keighley, *J. Appl. Polym. Sci.*, **19**, 2309 (1975).
9. T. Alfrey, *Chem. Eng. News*, **43**, 64 (1965).
10. T. Alfrey, E. F. Gurnee, and W. G. Lloyd, *J. Polym. Sci., Part C*, **12**, 249 (1966).
11. F. Jones, in *The Theory of Coloration of Textiles*, G. L. Bird and W. S. Boston, Eds., The Dyers Company Publications Trust, England, 1975.
12. J. H. Dumbleton and T. Murayama, *Kolloid-Z.*, **220**, 41 (1967).
13. R. P. Jamdagni and N. K. Chaudhuri, in DAE Symposium on Industrial Polymers and Radiation, Vallabh Vidyanagar, India, Feb. 1979.
14. H. Arimoto, *J. Polym. Sci., Part A*, **2**, 2283 (1964).
15. D. R. Holmes, C. W. Bunn, and D. J. Smith, *J. Polym. Sci.*, **17**, 159 (1955).
16. G. Giorgio, F. Annamaria, Z. R. Francesco, Z. Roberto, and C. Pietro, *Makromol. Chem.*, **175**, 953 (1974).

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