Modification of Nylon 6 Using Sulphuryl Chloride

D. S. VARMA & THOMAS EAPEN
Fibre Science Laboratories, Indian Institute of Technology, New Delhi 110 029

Received 9 December 1975; accepted 2 January 1976

Nylon 6 fibres were modified by reacting them with sulphuryl chloride in benzene. The extent of reaction was evaluated by measuring the increase in the weight of modified samples. The effect of duration of the reaction, reagent concentration, temperature and atmosphere was investigated, and the physical characteristics of the modified fibres were compared with those of the parent fibre. There was a marginal increase in the density and moisture regain of the modified samples with increase in add-on, while a decrease was observed in breaking strength and modulus. There was no appreciable change in elastic recovery and elongation, but a slight improvement in the thermal stability of the modified fibres.

Crosslinking of nylon 6 fibres with a bifunctional reagent improves their properties\(^1\). Disulphide bonds in wool and sulphur cross-bonds in vulcanized rubber impart unique properties to these materials. Chlorosulphonation of polyethylene\(^2\) gives good elastomeric properties. It was, therefore, expected that sulphuryl chloride may improve the physical properties of nylon 6.

Sulphuryl chloride can react either with the amide group \(-\text{NH-CO-}\) or carboxyl group \(-\text{COOH}\) or the free amino group \(-\text{NH}_2\). In the present study, nylon 6 fibres were treated with sulphuryl chloride in benzene medium. Samples with different amounts of crosslinks were prepared and the various physical properties were studied.

Experimental Procedure

Nylon 6 fibres obtained from J. K. Synthetics Ltd were Soxhlet extracted with petroleum ether. Sulphuryl chloride (BDH grade) was distilled before use.

Crosslinking method — The reaction with sulphuryl chloride was carried out at different temperatures for different durations and at different concentrations, in benzene medium and air or nitrogen atmosphere. After the reaction, the samples were washed with pure dry benzene to remove excess reagent and then again Soxhlet extracted for 6 hr. The samples were then dried for 2 hr at a temperature not exceeding 110°C, stored in a desiccator overnight and then weighed. The difference in weights of the yarn before and after the reaction was used to calculate the percentage weight gain. These crosslinked samples were then used for studying the properties.

Study of physical properties — The viscosity of the nylon 6 parent yarn as well as crosslinked samples was measured in m-cresol at 80°±1°C using Ubbelhode viscometer. Density was determined using the density gradient column containing mixtures of xylene \((0.866 \text{ g/ml})\) and carbon tetrachloride \((1.595 \text{ g/ml})\) in different ratios. Moisture regain was measured by the desiccator method using anhydrous phosphorous pentoxide as the dehydrating agent. Birefringence of the filament was measured by the Beckline method using liquid paraffin \((n = 1.471)\) and \(\alpha\)-bromonaphthalene \((n = 1.660)\).

The denier was measured by cutting fixed lengths and weighing them on a balance. Breaking strength, elongation, etc. were determined from the stress-strain curves obtained on Instron. The specifications used were: gauge length 2.5 cm, and full scale load calibration 100 g. Elastic recovery tests were also conducted using Instron, with the following specifications: gauge length 5 cm, cross-head speed 5 cm/min, chart speed 100 cm/min, full scale load calibration 20 g, extension given 5%, relaxation time 30 sec and recovery time 60 sec. All these tests were performed at 65±2% RH and 20±2°C.

Thermogravimetric analysis was done using a Stanton model HT-D thermobalance in air. The samples were cut into small lengths and 20±2 mg fibres were taken for each run. The analysis was carried out from room temperature to 550°C at a heating rate of 6°C/min. Primary thermograms were obtained by plotting the percentage residual weight against temperature. Differential thermal analysis was also done at a heating rate of 6°C/min using Stanton Red Croft differential thermal analyser. The samples were powdered and 10±2 mg of pulverized fibres were used for each run.

Results and Discussion

Effect of treatment conditions on the extent of reaction — The effect of concentration of sulphuryl chloride on percentage weight gain was investigated by carrying out the reaction for 2 hr in benzene medium in the presence of air as well as nitrogen (Fig. 1). The rate of reaction was higher in air atmosphere. At low concentration of the reagent, the reaction was slower. The percentage weight gain at a fixed time may be considered as the rate of reaction. A plot of log rate vs log conc. gave a straight line with a slope of 1 indicating that the rate of reaction is directly proportional to the concentration of sulphuryl chloride.

The effect of duration of the reaction on the percentage weight gain is evident from the data plotted in Fig. 2. It is seen that the percentage weight gain increases as the reaction proceeds for a longer period and then it seems to level off. The reaction was carried out at temperatures in the range 20–50°C. Increase in temperature resulted in high add-on...
(Fig. 3). The activation energy of reaction was calculated using Arrhenius plot and was found to be 8.9 kcal/mole. The temperature effect is considerable when the reaction is conducted at 40°C or above. The \( T_g \) of nylon 6, which is around 50°C, may be influenced and lowered down in the presence of chemical reagents. The extent of reaction obviously will be more above \( T_g \), when the polymer is in the rubbery state. In the glassy state, the diffusion of the reagent is less.

**Effect of chemical treatment on the fibre properties** — The viscosity measurement results are given in Table 1. The intrinsic viscosity of the treated samples is lower than that of the parent fibre, which may be due to the hydrolysis of nylon. During the reaction, HCl is produced, which may have hydrolysed the amide bond of the polymer.

The density, moisture regain and birefringence data are also given in Table 1. The density and moisture regain increase, whereas birefringence with the percentage add-on decreases. The increase in moisture regain is due to swelling, which in turn increases the density. A slight increase in moisture regain (4-5%) has been reported to increase the density. When sulphuryl chloride reacts with nylon 6 fibres, swelling takes place, pushing the molecules apart, so as to accommodate the bulky SO₂ groups between the chains. The resulting distortion caused by the swelling of the fibre sets up internal stresses which influence the moisture regain. The decrease in birefringence may be due to the disorientation of chains, which may be due to slack swelling of the nylon 6 fibres.

The stress-strain diagrams of nylon 6 treated samples are shown in Fig. 4(a) and (b). From the stress-strain curves, the breaking strength, elongation-at-break and initial modulus were noted and these data are given in Table 2. The breaking strength and initial modulus of all the modified samples lie below those of the parent fibre. The movement of the chains is restrained by the introduction of cross-bonds. Hence, there is less opportunity for chain mobility to help equalize the distribution of stress on the individual chains. This will create a high local stress, giving a chance of rupture. The breaking elongation is not changed appreciably.

The effect of crosslinking on elastic recovery is evident from the data given in Fig. 5. The elastic recovery of the modified samples is always higher.

---

**Table 1 — Effect of Crosslinking on the Physical Properties**

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Nylon- SO₂Cl₂</th>
<th>Wt. gain</th>
<th>( \eta )</th>
<th>Density</th>
<th>Moisture regain</th>
<th>Birefringence</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0</td>
<td>0</td>
<td>1.315</td>
<td>1.1485</td>
<td>4.31</td>
<td>0.05941</td>
</tr>
<tr>
<td>1</td>
<td>1:0.1</td>
<td>5.8</td>
<td>1.305</td>
<td>1.1610</td>
<td>4.35</td>
<td>0.05894</td>
</tr>
<tr>
<td>2</td>
<td>1:0.2</td>
<td>6.5</td>
<td>1.300</td>
<td>1.1665</td>
<td>4.37</td>
<td>0.05804</td>
</tr>
<tr>
<td>3</td>
<td>1:0.3</td>
<td>7.2</td>
<td>1.278</td>
<td>1.1685</td>
<td>4.39</td>
<td>0.05702</td>
</tr>
<tr>
<td>4</td>
<td>1:0.4</td>
<td>8.0</td>
<td>1.270</td>
<td>1.1655</td>
<td>4.41</td>
<td>0.05125</td>
</tr>
<tr>
<td>5</td>
<td>1:0.5</td>
<td>8.9</td>
<td>1.255</td>
<td>1.1720</td>
<td>4.40</td>
<td>0.04141</td>
</tr>
<tr>
<td>6</td>
<td>1:0.6</td>
<td>10.1</td>
<td>—</td>
<td>1.1890</td>
<td>4.44</td>
<td>0.04021</td>
</tr>
<tr>
<td>7</td>
<td>1:0.7</td>
<td>11.6</td>
<td>1.205</td>
<td>1.925</td>
<td>4.45</td>
<td>—</td>
</tr>
</tbody>
</table>
than that of the parent nylon 6 fibres. It is probably because of the stronger intermolecular and more flexible bonds caused by the SO$_2$ groups that bring the chains back to their original position after the removal of the load. However, in crosslinked nylon 6, strong covalent bonds are predominant, whereas in the parent nylon 6, only hydrogen bonds are acting in the amorphous regions.

The values of thermal properties are given in Tables 3 and 4. By thermogravimetric analysis, it was found that the parent nylon 6 starts decomposing at 180°C, whereas the crosslinked samples start decomposing only above 200°C, depending upon the weight gain. A sample which has got a weight gain of 10% starts decomposing only at 220°C. The initial stability may be due to SO$_2$ linkages. The IPDT values were calculated and the following stability order was observed: 1 > 3 > 4 > 2 > P > 5 > 7 > 6. The IPDT increases when the extent of crosslinking increases. The overall thermal stability was improved for samples having high percentage weight gain.

The differential thermograms were also obtained and these showed an endothermic shift in the region of the second order transition and a sharp peak at 215°C was observed, which was due to melting. The DTA trace showed a somewhat broad peak at 300°C and in some cases an exothermic peak above 400°C. Schwenker et al. reported the DTA thermograms for nylon 6. They observed exothermic and endothermic reactions similar to those observed in our samples. The influence of the crosslinking reaction on $T_g$ and $T_m$ is irregular. For example, in the modified samples, there is a peak at 276°C, which may be due to crosslinking.

Our results thus indicate that the reaction of nylon 6 with sulphuryl chloride is accompanied by predominant chain scission reactions. Cross-bond formation is indicated by the appearance of an additional peak in the DTA thermograms. As a result of hydrolysis, a deterioration in the properties is observed.

References