Recycling processes and products in nylon 6 fibre industry

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During the manufacture of nylon 6 polymer, about 8-10% of the caprolactam and its oligomers get converted into extractibles in the chips and during the manufacture of nylon 6 fibre, about 5-12% wastes are generated in solid form. It is essential that to make the production processes economically more viable, both the extractibles and the solid waste are converted into reusable products. This paper addresses this problem and describes the recycling processes and the products obtained therefrom.

Keywords: Caprolactam, Nylon 6, Waste recycling

1 Introduction

The world production of polyamide filaments increased1 from 3442 thousand metric tonnes in 1985 to 3789 thousand metric tonnes in 1989. In India, about 80,000 tonnes of nylon 6 yarn (40,000 tonnes of filaments and around the same quantity of tyre cord and fishnet yarns) is produced per annum.

The solid waste generated in a typical nylon 6 filament plant is around 10% (Table 1). Thus, about 7000-8000 metric tonnes of solid waste (nylon 6) is generated every year in India.

Nylon 6 used for the filament manufacture (polycaproamide) is formed by the hydrolytic polymerization of caprolactam. The process reaches a stage of equilibrium when about 90% of the reaction mass is the polymer, the remaining being caprolactam and its low molecular weight oligomers. It is desirable for economic reasons to recover the caprolactam and low molecular weight oligomers (extractibles) for reuse. Typical composition of the extractibles 2 is shown in Table 2. This composition is determined by the process conditions of polymerization and varies from 15% to 40% oligomers. A rapid accurate method for analysis of extractibles is provided by the high performance chromatograph3.

At times the cyclic oligomers are not recovered and recycled when about 4% caprolactam is lost as low molecular weight drain. These oligomers are sometimes recovered along with the solid nylon 6 waste and reused.

The solid fabric waste increases with the number of operations, the volume depending on the spun-denier, number of stoppages, etc. and can be 6-12% on the basis of dried chips. The various possibilities of reduction of waste during nylon 6 filament manufacture have been reviewed4.

The present article deals with the waste generated during the manufacture of nylon 6 polymer and filament yarn under the following heads: primary recycling of nylon waste, depolymerization of solid waste, depolymerization of oligomeric waste and recovery of caprolactam. In all cases, reference is made to the various processes described in the literature.

Table 1 - Solid waste generated in a typical nylon 6 plant

<table>
<thead>
<tr>
<th>Operation</th>
<th>Waste %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymerization/drying</td>
<td>0.8</td>
</tr>
<tr>
<td>Filament spinning</td>
<td>3.0</td>
</tr>
<tr>
<td>Draw-twisting</td>
<td>1.9</td>
</tr>
<tr>
<td>Texturing</td>
<td>1.0</td>
</tr>
<tr>
<td>Coning/rewinding</td>
<td>3.0</td>
</tr>
<tr>
<td>Packing</td>
<td>0.2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>10.0</strong></td>
</tr>
</tbody>
</table>

Table 2 - Typical composition of polycaproamide extractibles 2

<table>
<thead>
<tr>
<th>Extractible</th>
<th>Water extract</th>
<th>Methanol extract</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caprolactam</td>
<td>7.1</td>
<td>7.5</td>
</tr>
<tr>
<td>Linear oligomers</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>Dimer</td>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>Higher cyclic oligomers</td>
<td>1.6</td>
<td>1.7</td>
</tr>
<tr>
<td><strong>Total extractibles</strong></td>
<td><strong>9-10</strong></td>
<td><strong>10-11</strong></td>
</tr>
</tbody>
</table>
2 Primary Recycling

Unlike polyester waste, solid waste of nylon 6 (fibres, yarns) cannot be easily recycled to produce filament yarn since nylon 6 gets oxidized easily during storage and with the entrapped air in the voluminous fibrous wastes at elevated temperatures of melting, giving gels in the melt. Hence, the solid waste is usually depolymerized into the monomer for reuse. The solid waste is contaminated with spin finishes, coning oils, titanium dioxide, antioxidants, heat stabilizers, dyes, etc. The finishes and oil can be removed by washing with detergent solutions. It is possible to omit the washing process for the waste materials recovered by re-extrusion since high boiling impurities such as oils, spin finishes, etc. are removed by venting, leaving only non-volatile residues. Thus, it is advantageous to carry out the washing treatment only if an alternative method of removal of such impurities or their depolymerized products is not available. Therefore, the washing process is followed rarely in practice.

A suitable mill is used to grind the fibrous waste. By means of a pneumatic conveyor the milled fibre waste is passed over to the forced feeding system with simultaneous drying. The feeder supplies the waste to the extruder with precise heating of the extruder-screw and central cooling arrangements. The melt is then filtered, degassed and discharged to give chips of standard dimensions which can be blended with the virgin granulates without running the risk of separation. The throughput of the extruder increases considerably if the waste is thoroughly dried. Additives can be introduced during the extrusion process to get injection moulding-grade product. The melt may be added continuously to the depolymerization unit to get caprolactam (as discussed later). By the remelting methods such items as tough heels for ladies shoes or machine parts can be made. Nylon 6 yarn or plastic materials are manufactured by polymerization of 2-90 parts caprolactam with 98-10 parts of clean reusable nylon 6 waste having relative viscosity (RV) equal to or more than 2.2 (1 g/100 ml H₂SO₄, 25°C) in the presence of 5-10% aqueous phosphoric acid for 3-8 h at 215-230°C in an atmosphere to get polycaproamide having RV of 2.60 and polydispersity of 0.96 (ref. 9).

The clean waste can be converted into soluble nylon by reacting it with formaldehyde in a solvent. The film-forming properties of the soluble nylon improve with the higher fibre viscosity and, therefore, tyre cord polymer and waste give a better product.

Various solvent systems have been used to convert the solid nylon 6 waste into fine powder. Boiling the waste with ethyl alcohol under a pressure of 15 atmospheres and cooling give fine powder. 18% hydrochloric acid or 33% sulphuric acid at room temperature under stirring are also claimed to give powder. The solution is filtered, precipitated with water, centrifuged, washed, dried and finally ground. Ammonia solution is used as a precipitating agent. Such powders are added directly to the polymerization feed mixture.

Caprolactam is a good solvent for nylon 6 and up to 30% polymer can be dissolved in hot melt of caprolactam. Nylon 6 waste is dissolved in caprolactam-oligomer solvent and precipitated after filtering titanium dioxide in the waste to get powdered nylon 6 without much loss of degree of polymerization. Such powders are used for coating of metals by fluidized-bed technique.

High molecular weight nylon 6 powder with low COOH end group concentration and fine particle size (< 300 μm) has been produced from the nylon 6 waste (bright; free from TiO₂, finishes or colour) using a mixture of solvent and non-solvent to dissolve and to precipitate the nylon 6. Formic acid-acetic acid is a suitable pair of solvents. The powder is used for chromatographic separation of natural products.

A high boiling solvent (DMF) can be used to clean the waste and to dissolve the cleaned waste by carrying out the operation at two temperatures. At low temperatures (70-100°C), the impurities in the filament waste dissolve without affecting the nylon 6. The cleaned polymer is then dissolved in fresh solvent at elevated temperatures. The solid fibrous waste has also been used for removal of organometallics from wash waters when they are adsorbed by the nylon 6.

3 Depolymerization

Nylon solid waste is treated with water to get a product with a low degree of polymerization. The waste is charged to an autoclave, the air within is swept with nitrogen, and steam is admitted to the surrounding jacket. The polymer hydrolyzes slowly into the desired degree of polymerization for reuse. This process is rarely used as the product is not clean and pure enough to give a polymer of acceptable properties. Generally, the waste is depolymerized to give the monomer caprolactam or aminocaproic acid.

3.1 Depolymerization of Solid Waste

Nylon 6 solid waste is converted into caprolactam by heating with superheated steam to 200-400°C if necessary under pressure, in the presence of non-volatile organic or inorganic acids and alkalies, pref-
erably in 3-15:1 weight ratio of waste with acid/alkali hydroxide. Fresh waste is added along with the acid/alkali hydroxide as the caprolactam distils off with the steam. The waste may be in the form of lumps, chips, fibres, strands or may be a melt which is added continuously. The rate of depolymerization is dictated by the available surface area per unit weight of the waste and the fine structure of the fibrous material. When the thermal splitting process is started in the presence of caprolactam-H$_3$PO$_4$ (a compound formed by heating equimolar quantities of caprolactam and phosphoric acid), significant improvements in the purity of caprolactam are achieved. Separation of caprolactam molecule is possible from any part of the polymer chains as a result of an intermediate exchange reaction. The nature of the mol. wt. regulators or the chain terminators has little effect on the depolymerization process. Cyclic dimer exhibits very low reactivity because of the conformational stability of the ring and the electrostatic interaction of the closely located amide groups. The caprolactam formed should be removed efficiently from the reaction zone to displace the polymer-monomer equilibrium in the direction of monomer formation.

The alkali-catalyzed depolymerization reaction proceeds rapidly at 250°C. Besides caprolactam, great amounts of impurities are produced, the removal of which is very troublesome. At lower temperatures, the velocity of distillation of caprolactam depends on the extent of vacuum. Such processes are, therefore, rarely used commercially. Acid catalysts are found to give purer caprolactam than alkali catalysts. Boric acid (H$_3$BO$_3$) is reported to be more efficient than phosphoric acid; the decomposition rate is faster, handling of crystalline H$_3$BO$_3$ is easier and safer, and the corrosion of the apparatus is less severe. Boric acid (1%) at 280-290°C with superheated steam at 400°C under ambient pressure gives good conversion.

Caprolactam is recovered from nylon 6 waste in good yield by passing superheated steam through the molten mass at 225-350°C. A mixed phosphoric acid-boric acid catalyst at 0.1-5.0 wt % based on the polymer, is used. The steam containing caprolactam is condensed and the solution is worked up to get pure caprolactam. A concentration of the catalyst in the range of 0.3-1.0 wt %, based upon the polymer, gives 93-95% caprolactam recovery.

As an example, 150 kg nylon 6 waste is heated in a depolymerization reactor with 0.25% H$_3$BO$_3$ and 0.25% H$_3$PO$_4$ at 230°C. Superheated steam at 380°C is passed into the fused mixture and vapours condensed as usual to give cracked liquor containing 10-40% caprolactam. After 4 h, the reactor is recharged and the process is repeated until the concentration of caprolactam in the liquor drops to 1%.

The depolymerization can also be carried out in the presence of phosphoric acid alone. The caprolactam distils off along with the steam. Non-volatile matter such as titanium dioxide, inorganic salts, tar products of side reactions, antioxidants, stabilizers, etc. accumulate in the depolymerization reactor, slowly building up their concentration in the cracking mass. Some of the reaction mass is, therefore, drained at regular intervals of time to maintain the levels of inorganics (ash content) and impurities in the reactor. After a period, the entire mass is drained and the reactor is thoroughly cleaned before reuse. The frequency of the cleaning operation is decided by the amount of incoming inorganic matter, nature of nylon 6 waste, presence of antioxidant, dyes, spin finishes, dust and occasional unwanted fibrous waste, apart from the reaction conditions and the volume and frequency of draining. Less than 1% of the total nitrogenous body is lost during draining and cleaning processes. Caprolactam and phosphoric acid from the depolymerization residue and drainings are treated with water at 1:1 to 1:8 ratio and 60-90°C (ref. 22). The residue and the drainings are calcined, boiled with water and the mass is filtered to remove carbonized material. Phosphoric acid and its sodium salt are extracted with organic solvent.

3.2 Depolymerization of Oligomeric Waste

The extractibles in wash water from polycaproamide chips contain roughly 70-75% caprolactam and 25-30% oligomers (Table 2). The caprolactam in the mixture is separated by various techniques. The water is evaporated and the solid mixture is heated with steam at 18-20 kg gauge pressure to give a melt at 180-190°C. The melt is passed at 8.16 kg/h into a thin layer evaporator (bottom, 305°C; top, 250°C) and caprolactam (6.2 kg/h) with oligomer content <0.5% is distilled. The bottom product withdrawn at 1.95 kg/h contains practically no caprolactam.

In another process, the concentrated wash water is fed to a wiped film evaporator at 200-300°C and 10-250 mm Hg pressure, separating the wash water contents into an overhead stream of water and caprolactam, and bottom stream of oligomers containing caprolactam. Caprolactam from the overhead stream is recovered. The caprolactam in the bottom stream is stripped at 230-290°C with superheated steam. The oligomers are decomposed to caprolactam which is stripped with superheated steam. The recovery of caprolactam is improved in the
Caprolactam-oligomer mixture from the wash water is distilled in the absence of NaOH to recover crude caprolactam; the residue is heated in the presence of phosphoric acid and the caprolactam thus formed is steam distilled. The crude caprolactam is fractionally distilled in the presence of phosphoric acid and the caprolactam thus obtained is distilled in the absence of water in a multi-stage process. The wash water containing the mixture of caprolactam and oligomers is usually mixed with caprolactam or its solution to prevent the deposition of solids on the surfaces of the evaporator, pumps, pipes, etc. Thus, an aqueous solution of caprolactam and oligomers mixed with the wash water to increase the proportion of caprolactam in the mixture, thus preventing the precipitation of solids during evaporation, concentration and distillation of caprolactam. The bottoms are then sent for cracking the oligomers.

In another process of direct recycling of extractibles to get the polycaproamide, a mixture containing 30 parts of oligomers, 470 parts caprolactam and 15 parts water is heated for 80 min at 260°C at 10 kg/cm² pressure in the first reactor to give polycaproamide of low degree of polymerization. The mixture is flash-evaporated at 280°C in a second reactor to increase the degree of polymerization.

Oligomers are depolymerized into pure caprolactam by passing the oligomers (liquid or solid) through a fluidized bed of Al₂O₃ catalyst with steam at 290-400°C. Aluminium oxide is calcined at 800°C and has average particle size of 0.2-0.8 mm. It is heated to 320°C and fluidized with nitrogen (2500 litres/h) at 360°C. For over an hour, oligomer-caprolactam melt (30:70) is passed through the fluidized bed in a nitrogen stream (1500 litres/h) with 600 g steam added hourly for 4.5 kg oligomers to get pure 4.32 kg caprolactam. As the water vapour content of the catalyst increases, the yield of caprolactam increases from 78% to 98% (ref. 31).

The oligomers can be converted into caprolactam by the acid hydrolysis process using phosphoric acid and superheated steam. The conversion is quantitative and the recovered caprolactam is of very high purity. However, hydrochloric acid or sulphuric acid fails to give caprolactam from the oligomers. Thus, it is possible to recover caprolactam from the total extractibles quantitatively by recovering free caprolactam by steam distillation and hydrolyzing oligomers into caprolactam and steam distillation.

Caprolactam is recovered by heating the distillation residue in the presence of high boiling hydrocarbons and NaOH at 250-500°C and continuously removing the caprolactam from the reaction mixture off-gases. For example, the distillation residue (100 parts) containing 3% caprolactam and 5.8% NaOH is mixed with 200 parts technical-grade white mineral oil and heated to 350°C under nitrogen. The off-gases are condensed producing caprolactam.

**4 Recovery of Caprolactam**

The caprolactam distilled from the extractibles is pure enough for reuse without any purification treatment. However, it is a practice to mix the wash water with the cracked liquor obtained from the solid waste and to give purification treatments before recovering the caprolactam. Various acidic and basic impurities are formed by the degradation of the polycaproamide and spin finishes on the fibre waste during the depolymerization process. As the temperature of depolymerization increases, the rate of side reactions increases, giving black tarry oil, volatile bases, and other impurities in large volumes. The recovered caprolactam must meet the specifications of Permanate Number (Pm No.), volatile bases (VB), hazen colour, UV transmittance, solubility point, turbidity, etc. so that it can be used for polymerization.

A number of methods have been developed for the purification of caprolactam. Recrystallization and solvent extraction of caprolactam are generally used to get caprolactam of very high purity during its manufacture. Caprolactam can be extracted from its aqueous solutions by a membrane-solvent extraction process. The dissolved caprolactam is separated by a membrane from the extraction solvent (chloroform or tetrachloroethane) which is immiscible with water. The membrane is made up of hollow fibre of 40-500 µm diameter and 10 µm wall thickness with diffusion efficiency 1 x 10⁻⁴ cm²/s (ref. 33).

Solvent extraction techniques have also been used
to purify aqueous solutions of caprolactam by extracting colour, oxidizable impurities and oily matter\textsuperscript{34,35}. Solvent used for the extraction must be immiscible with water, a good solvent for impurities and oil, a non-solvent for caprolactam, and economical and non-toxic. A petroleum fraction (kerosene, diesel) is found to meet these specifications and removes the oily impurities. The solvent extract thus obtained can be burnt to recover the processing costs\textsuperscript{35}.

It is possible to control the formation of oily impurities and to remove them by separating the layers in a settling tank of high height to diameter ratio.

### 4.1 Treatment with Resins

Ion-exchange resins have been used to purify aqueous solutions of caprolactam\textsuperscript{36}. Some such resins, e.g. Amberlite IR 45, Amberlite IR 120B and Diaion SA-20, are described in the literature\textsuperscript{37-40}. The usual steps in the purification process are oxidation of impurities, filtration, resin treatment and distillation. The distilled caprolactam may be further treated with Zeolite molecular sieves of pore diameter 4 Å for the removal of volatile bases and coloured contaminants\textsuperscript{31}.

Caprolactam is purified by stirring the melt or solution in an organic solvent or by continuously passing through a vertical column containing molecular sieves. Resins get coated by the oily matter coming from the cracked liquors and soon become ineffective, needing frequent cleaning and regeneration. It is, therefore, imperative to clean the cracked liquors from oily impurities before resin treatments. An effective method of removing all the oily matter is the treatment with active carbon and filtration of the sludge. Removal of oil by settling, adsorption on a special resin column, and such other methods followed by filtration give clean caprolactam solution suitable for the resin treatment. Soiled resins are cleaned by a solvent, emulsifying agent solution, and hot water before their regeneration.

Ion-exchange resins remove all the ionic impurities and filter off colloidal floating particles, apart from the colouring impurities. The alkali-metal salts formed in the permanganate oxidative treatments are removed in the cation-anion exchange resin treatment. This improves the distillation process and the drainings from the bottom of the distillation column are almost free from ionic impurities (except the traces of NaOH added during the distillation). The treatment of the drained material for caprolactam recovery becomes easier, economical and more effective. The bottoms are usually cracked along with the solid wastes.

### 4.2 Treatment with Adsorbents

Purification of caprolactam is carried out prior to distillation using both acidic and alkaline (pH) conditions for adsorption on activated carbon on the assumption that an equal number of COOH and OH groups are present on the surface of the carbon\textsuperscript{42,43}. Thus, anionic and cationic impurities are removed by the treatment of activated carbon. The activity of carbon increases significantly on heating prior to its use, coconut charcoal giving the best results. Wood charcoal calcined at 900°C for 1 h gives good results\textsuperscript{44}. Removal of charcoal by filtration is easier if the solution is acidic. Alkaline solutions are filtered under vacuum.

Adsorption is used to remove traces of caprolactam from water. Activated charcoal adsorbs the caprolactam from its very dilute solutions. The carbon is treated with acetone to recover the adsorbed caprolactam and with superheated steam to activate for reuse. This process has been used to reduce the concentration of caprolactam in waste water from 433 mg/litre to 45 mg/litre\textsuperscript{45}.

### 4.3 Treatment with Oxidizing Agent

Impurities in aqueous caprolactam solutions have been destroyed by oxidative treatments. Passing of ozone through the caprolactam solution followed by fractional distillation gives caprolactam having Pm No. 3000 compared to zero for the untreated one. The ozone leaves no ionic impurities and, therefore, does not burden the ion-exchange resins in the following treatment\textsuperscript{46}. Most commonly used oxidizing agent is KMnO\textsubscript{4}. The treatment in neutral medium at 40°C is recommended; the alkaline or acidic medium induces oxidation of caprolactam to isocyanates. This reaction proceeds faster at pH above 7 because of the saponification of isocyanates and shifting of the reaction equilibrium\textsuperscript{47}. The incorporation of active carbon containing substantial amount of Fe\textsuperscript{3+} is also undesirable since it leads to excessive consumption of KMnO\textsubscript{4}. However, the caprolactam obtained after such a treatment and fractional distillation shows improved Pm No. Alkaline consumption during fractional distillation is decreased and the yield increased by conducting the first stage of distillation at pH 4.5-6.9 and treating with KMnO\textsubscript{4} and active carbon in an acidic medium prior to distillation\textsuperscript{48}.

Oxidative treatments are given usually after concentrating the cracked liquor to 40-60%. The concentrated solution after KMnO\textsubscript{4} treatments and calcium oxide addition\textsuperscript{49} and filtration is further concentrated to 98-99% and dehydrated to distil caprolactam. Addition of freshly prepared potassium metasilicate gives good caprolactam yields in short times.

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