

Depolymerization of Nylon 6 Waste Fibers

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Received 7 December 2004; accepted 8 April 2005

DOI 10.1002/app.22775

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The depolymerization of nylon 6 was carried out with various solvents, such as formic acid, hydrochloric acid, and sulfuric acid, followed by heating under reflux for different times. From the polymer dissolved and refluxed in formic acid, degradation products with different ranges of molecular weights were collected by fractional precipitation, with small lots of distilled water added as a nonsolvent. The characterization of different fractions was carried out by the measurement of the viscosity-average molecular weight, the

number-average molecular weight, and the number of amino end groups. The presence of the monomer, aminocaproic acid, was confirmed by thin-layer chromatography in the case of hydrochloric acid treated nylon 6. With a strongly acidic ion-exchange resin, the monomer was separated in its purest form, and the melting point was noted. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 186–190, 2006

Key words: nylon; monomers; recycling; viscosity

INTRODUCTION

A huge amount of waste is generated during the manufacture of synthetic textile fibers and filaments and also when products made from them are discarded after their utilization. Because these are nonbiodegradable, their disposal creates many environmental problems. The disposal of solid waste into landfills has become increasingly prohibitive because of the high cost involved, the legislative pressures, and public opinion. Growing environmental awareness and reductions in available landfill capacity have prompted recycling programs in most developed countries.¹

Moreover, synthetic polymers are produced from the limited, nonrenewable resource petroleum, the supply of which is going to become exhausted in the near future. The conservation and efficient use and reuse of materials thus have become dominant themes of the industry. The waste generated from synthetic fibers is relatively pure and does not have much foreign material, and so the recovery appears to be simple.²

Probably most people of the world today have daily contact with nylon in one form or another. In general, clothing such as stockings, socks, saris, shirts, blouses, sweaters, cardigans, sportswear, and swimwear are produced either with nylon alone or with its combinations with other yarns. Besides this, nylon 6 has captured a large share of the market of engineering

plastics, such as high-tenacity yarns for fishnets and as reinforcing materials for pneumatic tires, parachutes, and conveyor belts.³

During the manufacture of nylon 6, a considerable amount of waste is generated at various stages of the polymerization, right from the autoclave, VK tubes, and cutters to spinning, texturing, winding, and packing. The physical forms may be polymeric lumps, entangled and broken filaments, rejected bobbins, and so forth.

Not enough literature on nylon 6 recycling is available. Methods used for the recovery of economic value from nylon 6 wastes can be broadly classified under two categories: mechanical and chemical.⁴ Mechanical recycling involves the remelting and spinning of coarse filaments.

The rationale for chemical recycling begins with the view that although mechanical melt recycling will continue to play a major role, it cannot by itself become the most economical, long-term solution to the total resource recovery issue. Regardless of where one starts, mechanical recycle tends to end up in a lower value product because of some contamination and an inevitable loss of properties.

The recycling of polymeric waste to the monomer is generally carried out in a high-temperature and high-pressure environment in the presence of catalysts; this has the obvious disadvantages of sophisticated equipment, difficult process control, and monomer separation and purification afterwards. Superheated steam in the presence of acids and alkalis may also be used for depolymerization under pressure. However, the sublimation tendency of the oligomers produced or the use of corrosive catalysts poses problems. Dmit-

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rieva and coworkers⁵⁻⁸ reviewed the catalytic depolymerization of nylon 6 waste with superheated vapor.

This communication presents the results for the depolymerization of nylon 6 waste fibers through dissolution in various acids, such as formic acid, hydrochloric acid, and sulfuric acid, and then through the heating of the solutions under reflux for different times. Fractions of the degraded polymer of various molecular weight ranges in formic acid were segregated by fractional precipitation with successive additions of small lots of distilled water as a nonsolvent. The characterization of different fractions was carried out by the estimation of the viscosity-average molecular weight (M_v), the number-average molecular weight (M_n), and the number of amino end groups. The presence of the monomer was confirmed by thin-layer chromatography (TLC). With a strongly acidic ion-exchange resin, the monomer aminocaproic acid (ACA) was separated in its purest form.

EXPERIMENTAL

Materials

Nylon 6 waste fiber was used.

Formic acid, sulfuric acid, and hydrochloric acid, obtained from Merck, were Laboratory Reagent-grade.

Thymol blue was used as an indicator. Bromocresol green was used to prepare the locating spray for TLC via mixing with sodium hydroxide and ethanol.

Indion 130, procured from Ion Exchange (India) Pvt., Ltd. (Mumbai, India), was used as a cation exchanger in a strongly acidic form.

An ammonia solution was used to elute a dilute solution of ACA from the resin column.

Auxipon NP (Auxichem, Ltd., Mumbai, India) was used as a nonionic detergent.

Purification of nylon 6 waste

Nylon 6 fiber waste was treated with a 1 g/L solution of a nonionic detergent at 80°C for 20 min. It was rinsed thoroughly with water to remove any surface impurities and then dried in air.

Depolymerization of nylon 6

Finely cut nylon 6 fiber waste (5 g) was dissolved in 75 mL of 90% formic acid at room temperature (30°C). Similarly, 4 g of nylon was dissolved in 100 mL of different concentrations of hydrochloric acid and sulfuric acid with gentle warming. All these solutions were heated under reflux for different times up to 20 h to obtain acid-hydrolyzed products.

Fractional precipitation

Different low-molecular-weight fractions of the degraded polymer were precipitated out by the addition

of 20 mL of distilled water as a nonsolvent to the aforementioned solutions gently stirred for 30 min and then left at 0°C overnight. Fraction I was filtered through a G4 sintered glass crucible and dried in air. The fraction II precipitate was obtained in a similar manner from the aforementioned filtrate. The addition of the nonsolvent was continued further until the traces of the precipitate became invisible. These fractions were subjected to characterization.

Measurement of the viscosity

The precipitates of fractions I and II were dissolved in 90% formic acid to prepare a 1% solution. The absolute viscosities of the solution and solvent were measured with an Ostwald U-tube viscometer (J-Sil Laboratory Glasswares, Agra, India), and the relative viscosity (η_{rel}) was calculated as follows:

$$\eta_{rel} = \frac{\text{Flow time for solution}}{\text{Flow time for solvent}}$$

Determination of the molecular weight

M_v was determined with the following formula:

$$M_v = (\eta_{rel} - 1) \times 96 \times 113$$

End-group analysis

One gram of the precipitate was dissolved in 25 mL of a phenol/methanol mixture (70:30 w/w) via refluxing for 30 min. The contents were cooled and titrated against 0.02N HCl with thymol blue as an indicator. A blank was also run:

Concentration of amino end groups ($\mu\text{equiv/g}$)

$$= \frac{(A - B) \times \text{Normality of HCl} \times 1000}{\text{Weight of the sample}}$$

where A is the volume (mL) of 0.02N HCl required for titration with the sample and B is the volume required for the blank.

M_n was calculated with the following relationship:

$$M_n = \frac{10^6 \times n}{\text{End groups } (\mu\text{equiv/g})}$$

where n is 1 or 2 according to whether the measured end groups are at one or both ends of the polymer molecule.

Chromatographic analysis

The acid-hydrolyzed product was dried over solid sodium hydroxide, with a vacuum applied, and then

dissolved in water. This was run on Kieselgel G thin-layer plates with an *n*-propanol/ammonia solution (7:3) as an eluent. Good separation was achieved, and the spots were viewed by the spraying of a bromocresol green solution onto the plates. The locating spray was prepared as follows: 0.05*N* sodium hydroxide was prepared by the dissolution of sodium hydroxide (1 g) in water (500 mL). Bromocresol green (0.1 g) was dissolved in a mixture of 0.05*N* sodium hydroxide (2.9 mL) and 90% ethanol (5 mL) with warming. The solution was made up to 250 mL with 20% ethanol to give a final concentration of 0.04%.

The R_f values were calculated as follows:

$$R_f = \frac{\text{Distance traveled by substance}}{\text{Distance traveled by solvent front}}$$

Purification and crystallization of ACA

ACA was separated by the passage of the acid-hydrolyzed solution through a commercial cation exchanger (Indion 130). To prepare the ion-exchange column, the resin was first soaked in water; it became swollen, and its surface cracked. A small amount of glass wool was placed inside a glass tube with a 0.7-cm internal diameter. The swollen resin was filled in the tube to make a 15-cm-high column. A small amount of glass wool was placed on the top. An acid-hydrolyzed solution was passed through this column at a rate of 2.5 mL/min. The column was washed with excess distilled water until the eluent was free from traces of chloride or sulfate ions. The dilute solution of the hydrolyzed product was eluted by the passage of an excess amount of a dilute ammonia solution from the column. Up to half of the volume of the dilute solution evaporated, and the solution was allowed to crystallize by being left overnight in the refrigerator. The crystals were separated and dried by a stream of air.

The melting point was determined in an open capillary with a melting-point apparatus.

RESULTS AND DISCUSSION

Nylon 6 dissolves in acids, and upon the further heating of its solutions, it becomes depolymerized. In this work, nylon 6 was dissolved in different concentrations of various acids such as formic acid, hydrochloric acid, and sulfuric acid, and this was followed by the heating of the solutions under reflux for different times. Zaikov and coworkers^{9,10} carried out kinetic studies on the breakdown of nylon 6 by hydrolysis in an aqueous solution of sulfuric acid. Because of heating, long-chain polymeric molecules became hydrolyzed, and chain scission took place. The size of the polymer chain thus was reduced. The nonsolvent, distilled water, was added in successive portions of 20

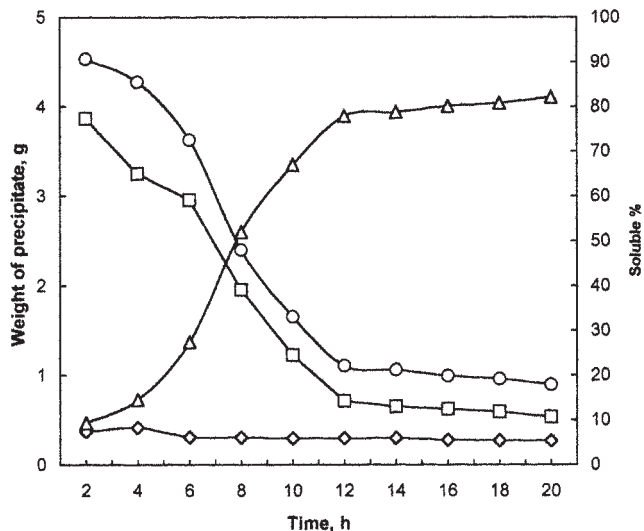


Figure 1 Effect of time on the different fractions, total precipitate, and soluble compounds: (□) fraction I, (◇) fraction II, (○) total precipitate, and (△) soluble compounds.

mL to the refluxing solution of nylon 6 at 2-h intervals to precipitate out different fractions of the depolymerized nylon 6.

When a small quantity of a nonsolvent is added to a polymer solution, it decreases the solvent power to such an extent that the molecular species bearing the highest molecular weight can no longer be held in solution and hence is thrown out of the solution as a precipitate (fraction I). Upon its removal by filtration and the addition of the next 20-mL portion of distilled water, the solvent power decreases further, and the fraction II precipitate of the next higher molecular weight species is generated. In this work, this procedure was continued until the precipitation of fractions III and IV, which were obtained in extremely small quantities and hence were not subjected to characterization studies. The total precipitate, however, comprised the weights of all four precipitated fractions of the depolymerized species collected at 2-h intervals of the refluxing of the polymer solution.

For 5 g of nylon 6 waste dissolved in 90% formic acid and refluxed up to 20 h, the data are plotted in Figure 1. With an increase in the time of heating, the fraction I precipitate and the total amount of the precipitate generated decreased and that of the water-soluble compounds increased steadily up to about 12 h of refluxing. Thereafter, until 20 h, the changes were only marginal.

Fraction II, having very low amounts, showed a steady and marginal decrease over the whole period of refluxing. The precipitate of fraction I collected after 2 h was 3.867 g, which decreased to 0.710 and 0.535 g at the end of 12 and 20 h of refluxing, respectively. For fraction II, the respective values were 0.370, 0.295, and 0.270 g. On the other hand, the concentration of water-

TABLE I
Data on the Analysis of Fraction I Obtained by the Fractional Precipitation of Nylon 6 Treated with Formic Acid

Treatment time (h)	M_v	M_n	M_v/M_n	End groups ($\mu\text{equiv/g}$)
0	12,914	10,204	1.27	98
2	4,773	4,717	1.01	212
4	3,797	3,788	1.00	264
6	3,254	3,185	1.02	314
8	2,061	2,016	1.02	496
10	1,848	1,812	1.02	552
12	1,627	1,595	1.02	627
14	1,302	1,259	1.03	794
16	1,085	995	1.09	1005
18	868	800	1.08	1250
20	759	680	1.12	1471

soluble compounds increased from 9.34 to 82.12% at the end of 20 h of refluxing.

Thus, in the case of formic acid hydrolyzed nylon 6, even after 20 h of refluxing, the complete degradation to its monomer, ACA, was not observed. This was confirmed from the chromatogram of the aqueous solution remaining after the removal of the precipitate, which gave more than one single spot, obviously because of the presence of different oligomers present.

Fraction I and fraction II precipitate contents were characterized, and the data are given in Tables I and II, respectively. Refluxing the polymer solution up to 2 h gave a sudden reduction in M_v and the weight-average molecular weight (M_w), and thereafter the decrease was steady. The initial end amino group content of 98 increased to more than double after the first 2 h, and at the end of 20 h of refluxing, it increased to 1471. The chain scission thus continued right from the beginning of reflux heating, leading to shorter and shorter chain fragments. The data on M_v and M_n in these two tables indicate that the original polymeric fiber waste with $M_v = 12,914$ and $M_n = 10,204$ was degraded to low-molecular-weight polymeric chains obtained in fraction I with respective values of 542 and 590 after 20 h of treatment. These values are not significantly different.

The variation in the length of the different polymeric molecules was quite high during the initial stage of refluxing the acidic solution (i.e., M_v/M_n was high). As the process of chain scission continued with an increase in the time, the shorter chain length molecules were very large in number. During the initial period of heating, the polymer solution, mainly long-chain molecules, were sliced. This caused the end-group content during the initial period of treatment to be less. As the time of heating increased, the shorter and shorter chain molecules, each one contributing to one end amino group, also started disintegrating. The end-group content, therefore, increased rapidly.

Textile synthetic materials are known to be polydisperse in nature, and the ratio M_w/M_n is taken as the index of polydispersity. The estimation of M_w requires sophisticated equipment. It has been reported that M_v is very close to M_w .¹¹ The ratio M_v/M_n was, therefore, considered to be an indication of polydispersity. The values in Tables I and II indicate that this ratio for the original nylon 6 polymer was 1.27, which after 2 h of refluxing was reduced to close to unity and thereafter remained nearly the same with only a slight increase. Thus, the larger polymeric molecules were degraded, and the ratio M_v/M_n remained almost constant (near to 1); this indicated that all the precipitated polymer fractions contained almost identical chain lengths.

Thus, the work using formic acid for the depolymerization of nylon 6 indicates that the ultimate degradation level of the polymer is not fully to the monomeric level, that is, ACA, but oligomers are also obtained that amount to about 10–15% of the original polymer.

The depolymerization of nylon 6 was also tried with hydrochloric and sulfuric acid. The dissolution of nylon 6 commenced only with 30% hydrochloric acid, and it was used between 30 and 60%. Similarly, 15% sulfuric acid was used for dissolving nylon 6. Sulfuric acid of a 10% concentration did not dissolve nylon 6, whereas concentrations of 20% and higher charred the polymer solution on heating.

The addition of any amount of distilled water as a nonsolvent to a polymer solution obtained with hydrochloric or sulfuric acid did not produce any precipitate, and the solution remained optically clear. This implies that the mineral acid hydrolyzed polymer solutions consisted of water-soluble compounds only, such as the monomer ACA and the soluble oligomeric compounds. It was reported by Goel and Seetha¹² that only a linear dimer has significant solubility of 1.8% at 25°C, whereas other oligomers are insignificantly soluble (<0.3%).

TABLE II
Data on the Analysis of Fraction II Obtained by the Fractional Precipitation of Nylon 6 Treated with Formic Acid

Treatment time (h)	M_v	M_n	M_v/M_n	End groups ($\mu\text{equiv/g}$)
0	12,914	10,204	1.27	98
2	4,556	4,464	1.02	224
4	3,471	3,448	1.01	290
6	2,820	2,710	1.04	369
8	1,519	1,504	1.01	665
10	1,410	1,399	1.01	715
12	1,302	1,290	1.01	775
14	1,085	1,010	1.07	990
16	976	905	1.08	1105
18	651	625	1.04	1600
20	542	580	0.93	1724

TABLE III
Data on the Conversion (%) of Nylon 6 to ACA with Different Acids

Treatment time (h)	HCl			15% H ₂ SO ₄ (v/v)
	30%	40%	50%	
4	93.25	94.00	90.15	78.75
6	91.00	90.35	91.00	71.15
8	91.50	89.55	90.50	68.00

The hydrolyzed solutions were subjected to TLC analysis with a mixture of *n*-propanol and ammonia (70:30) as an eluent. Only a single spot with an R_f value of 0.22 was observed for a solution of nylon 6 hydrolyzed with 30–50% hydrochloric acid, which corresponded to ACA.¹³ This also suggests that the depolymerized product was almost pure ACA and that other oligomeric compounds were present in significant amounts.

ACA can be separated and purified from a mixture of oligomers and other low-molecular-weight compounds with a cation exchanger (strongly acidic type). The results on the separation percentage of ACA are given in Table III.

After 4 h of treatment with 30% hydrochloric acid, the yield of ACA was 93.25%, which decreased slightly to 91.50% after 8 h of treatment. This may be attributed to repolymerization, upon prolonged heating, forming certain oligomers. A higher concentration of hydrochloric acid, up to 50%, did not show any significant variation in the amounts of ACA formed. Similar were the observations with 15% sulfuric acid. The melting point of the purified product was 203°C, which confirmed ACA.

CONCLUSIONS

Studies on the depolymerization of nylon 6 by dissolution and heating in formic acid, hydrochloric acid, and sulfuric acid indicate that formic acid depolymer-

izes nylon 6 into low-molecular-weight compounds of various chain lengths and that even after 20 h of refluxing, the depolymerization is incomplete. Different fractions of more uniform characteristics can be precipitated and segregated by fractional precipitation with distilled water as a nonsolvent. The chain lengths of the first fraction are much lower than those of the original nylon 6, and they are mostly uniform in nature.

Thus, it may be possible to recycle nylon 6 based high-tenacity tire cord yarn and fishing nets with higher molecular weight chains and reuse the depolymerization products after conversion to lower tenacity fibers for fiberfill in pillows, cushions, mattresses, and so forth. Furthermore, hydrochloric acid and sulfuric acid have been found to depolymerize nylon 6 fiber waste almost completely to ACA with high purity, and this presents further possibility of recycling. Because ion-exchange-separated ACA was found to be highly pure, it can be repolymerized either alone or in combination with virgin ACA.

References

1. Wolff, K. R. *Chemiefasern/Textilind* 1980, 30, 500.
2. Scheirs, J. *Polymer Recycling*; Wiley: Chichester, England, 1998; p xii.
3. Sharma, N. D.; Sharma, R. B. *Synth Fibers* 1989, 18, 6.
4. Sharma, N. D. *Text Asia* 1991, 22, 68.
5. Dmitrieva, L. A.; Speranskii, A. A.; Krasavin, S. A.; Bychkov, Y. N. *Khim Volokna* 1985, 4, 5.
6. Moran, E.; Francis, J. R. *Pat. WO 9408942* (1994).
7. Nakade, S.; Fujita, K. *Jpn. Pat. JP 6032775* (1994).
8. Crescentini, L.; Fisher, W. B.; Blackman, J. R.; Web, B. B.; Lilley, J. R.; Roy, J.; Decaprio, J. D.; Wagner, J. W. *Pat. KR 8600829* (1986).
9. Nechaev, P. P.; Moiseev, Y. V.; Zaikov, G. E. *Vysokomol Soedin Ser A* 1972, 14, 1048.
10. Nechaev, P. P.; Moiseev, Y. V.; Zaikov, G. E.; Petrova, T. E. *Izv Akad Nauk Ser Khim* 1972, 1, 33.
11. Taylor, G. B. *J Am Chem Soc* 1947, 69, 635.
12. Goel, I. N.; Seetha, K. N. *Synth Fibers* 1982, 11, 8.
13. Raven, D. J.; Earland, C. *J Soc Dyers Colour* 1970, 86, 313.