# Extrusion Freeforming of Nylon 6 Materials

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## INTRODUCTION

Numerous commercial rapid prototyping (RP) processes are capable of fabricating complex shaped components. These processes build prototypes "from the ground up" by first reducing a CAD design of the desired prototype to a series of geometrical slices followed by the precise sequential deposition of raw material layers upon one another. Unfortunately, these RP processes are limited to producing prototypes from polymers that exhibit inferior mechanical properties compared to commercial engineering thermoplastics. Consequently, there are significant advantages in extending the materials processing capabilities of RP technology into the realm of producing tough, high strength functional prototypes from engineering polymers.

## BACKGROUND

A possible method of fabricating high strength polymer prototypes utilizes extrusion freeforming techniques (EFF) where parts are built from a series of precisely deposited liquid monomer layers that are subsequently thermally polymerized to form the desired thermoplastic component (1). EFF monomer deposition is typically performed using a syringe pump fitted with a fine bore nozzle that is interfaced to a CAD based motion control hardware. A major advantage of freeforming liquid monomer compared to molten engineering thermoplastic feedstock is that the former have lower viscosity (which facilitates accurate dispensing) and do not exhibit many of the viscoelastic rheological problems encountered during extrusion of the latter (i.e. die swell) (2). It is necessary that the EFF resin used to fabricate these parts rapidly polymerizes to a high molecular weight thermoplastic in high yield. It is also necessary that the resin polymerizes with minimal shrinkage and reaction exotherm otherwise there may be significant stresses or poor adhesion present between the freeformed part layers.

A review of the literature reveals that caprolactam monomer satisfies the above EFF resin requirements since it is a low viscosity liquid when molten (86° C melting point) and readily undergoes ring opening polymerization to yield Nylon 6 polymer. This polymer is a thermoplastic that is used in a wide variety of structural applications including gears and pump impellers and bearing housings (3,4). In comparison to monomers used in other RP techniques (i.e. stereolithography acrylates) caprolactam also exhibits a lower polymerization exotherm. (- $\Delta H$ nylon = 10 kcal/mol     - $\Delta H$ acrylate = 18-25 kcal/mol) (5,6).

Rapidly polymerizable caprolactam resin is commercially available in bulk quantities (typically used in nylon casting & reaction injection molding (RIM) processes) and is primarily composed of molten monomer containing small amounts of sodium caprolactamate base and an N-Carbamoyl Caprolactam activator compound (7). Polymerization proceeds via an anionic ring opening mechanism presented below, whereby sodium caprolactamate base initially opens the lactam ring portion of the activator compound which in turn initiates caprolactam polymerization (8). ( See Fig. 1 below for reaction mechanism depiction.)
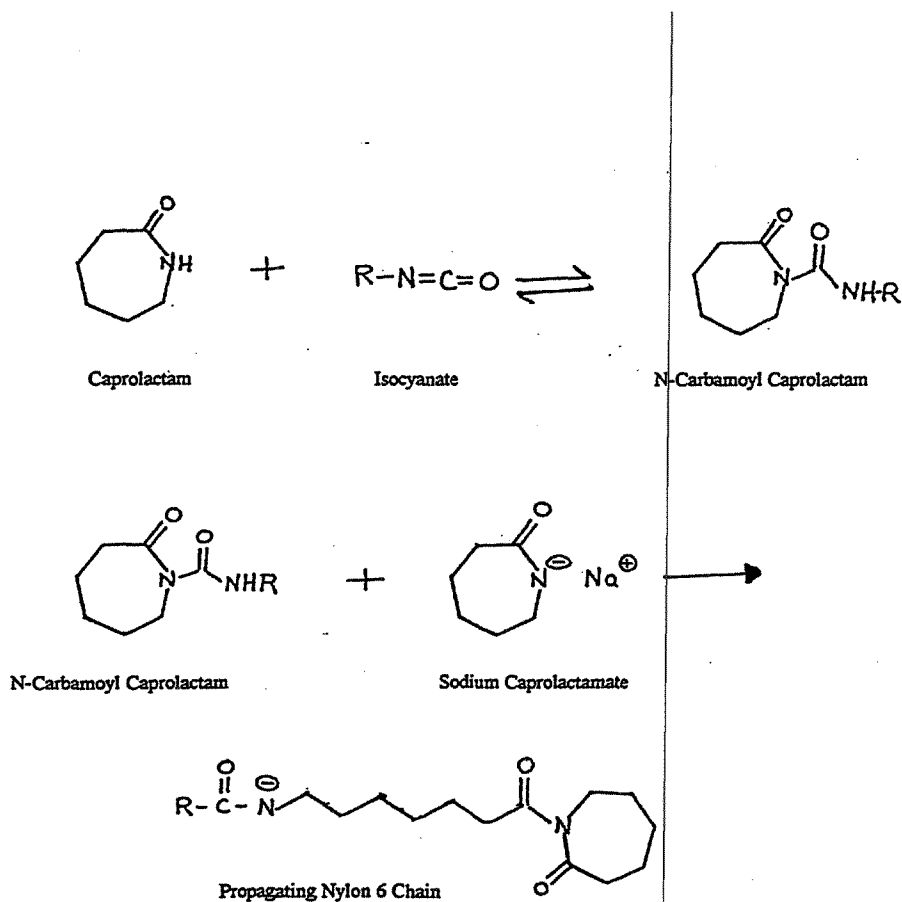
Figure 1. Anionic caprolactam ring opening polymerization reaction mechanism

N-Carbamoyl Caprolactam activators are a key component in the caprolactam resin since these compounds lower the activation energy and reaction temperature for Nylon 6 polymerization. Most commercial activators are multifunctional isocyanates which produce Nylon 6 polymer in > 96 % yield within a few minutes after heating the resin above 150° C (9).

## EFF Compatible Nylon 6 Resin Development

Despite its numerous advantages, the high reactivity and low shelf life of commercial caprolactam resins precluded their use in EFF processing due to their propensity to gel and clog the EFF apparatus syringe pump dispensing system. The resin had to be reformulated with an activator that was stable at the EFF pump reservoir temperatures (70° C) while simultaneously having the ability to polymerize the resin shortly after dispensing onto a resin curing platen heated at 165° C. Experiments were conducted with various isocyanate compounds to obtain a latent activator. Tetramethylxylxylene diisocyanate (TMXDI) and dimethylbenzyl meta-isopropenyl benzene (TMI) were two compounds found to be suitable EFF compatible latent polymerization activators. The cure properties of these two activators are summarized in Table I below.

## TABLE I TMXDI & TMI NYLON ACTIVATOR CURING CHARACTERISTICS

| ACTIVATOR | ISOCYANATE FUNCTIONALITY | TIME (MIN) REQ'D TO GEL RESIN @ 165° C | TIME (MIN) REQ'D TO GEL RESIN @ 70° C |
|-----------|--------------------------|----------------------------------------|---------------------------------------|
| TMXDI | 2 | 10 | 35 |
| TMI | 1 | 20 | 45 |

* Nylon resin composition: 30g caprolactam, 1 mol.% activator, 2 mol. % Na Caprolactamate

After determining EFF compatible latent activators, optimal curing conditions for the reformulated resins were determined by measuring the percent crystallinity and crystallization undercooling on cast Nylon 6 specimens using differential scanning calorimetry (DSC). The percent crystallinity within a cast sample varied directly with its modulus and strength while melt undercooling also varied directly with the melt viscosity and molecular weight of the Nylon 6 polymer present in each sample (10,11). The results from the DSC characterization of samples cast with TMXDI activator at 165° C for time periods ranging from 15 minutes to 4 hours are presented in Table II below. DSC results for a sample cast with half the amount of sodium caprolactamate base and TMXDI activator are also presented in Table II.

## TABLE II DSC RESULTS FOR TMXDI CAST NYLON 6

| Sample (Polym Temp-Time) | % Crystallinity | Undercooling Temp. T |
|--------------------------|-----------------|----------------------|
| 165-15 | 40 | 41 |
| 165-30 | 41.6 | 43 |
| 165-45 | 42.7 | 44 |
| 165-4hr. | 50.4 | 44.4 |
| 165-15 ½ TMXDI, Base | 48.5 | 47 |

* Nylon resin composition was similar to that given in Table I above

From the above results it can be seen that sample crystallinity and melt undercooling increased with reaction time indicating that the nylon polymer increases in molecular weight and crystallinity upon prolonged reaction. The molecular weight of the final nylon polymer was found to level off after a four hour reaction period. Decreasing the amount of sodium caprolactamate base and activator in the resin yielded a polymer product having both higher molecular weight and crystallinity. This too is expected since the anionic polymerization of caprolactam is believed to be a quasiliving process where polymer product molecular weight is inversely proportional to activator concentration (12). The mechanical properties of these samples were also determined using an Instron Model 1011 tensile testing apparatus. The tensile testing results are provided in Table III below.
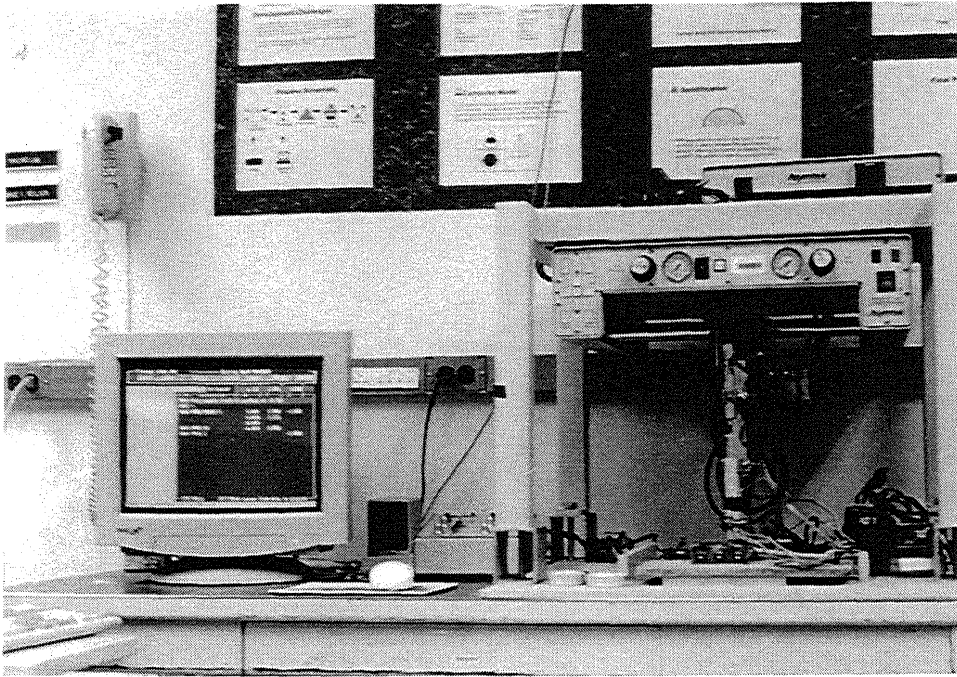
Figure 2. Photograph of Asymtek Fluid Dispenser used for nylon resin extrusion freeforming.
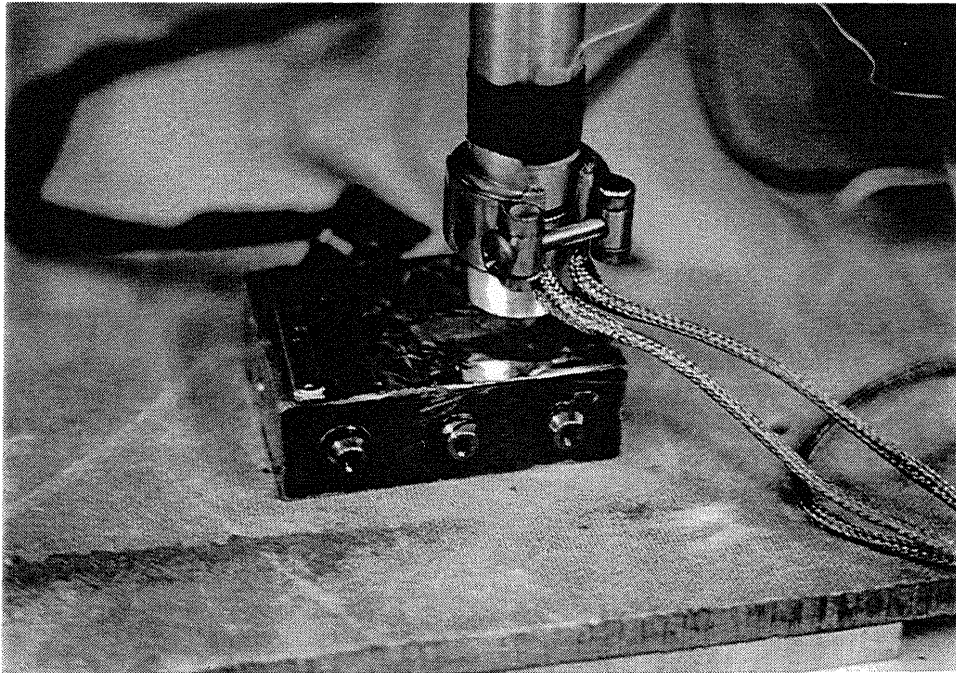


Figure 3. Photograph of Asymtek EFF apparatus syringe pump nozzle freeforming nylon resin onto a heated aluminum platen.
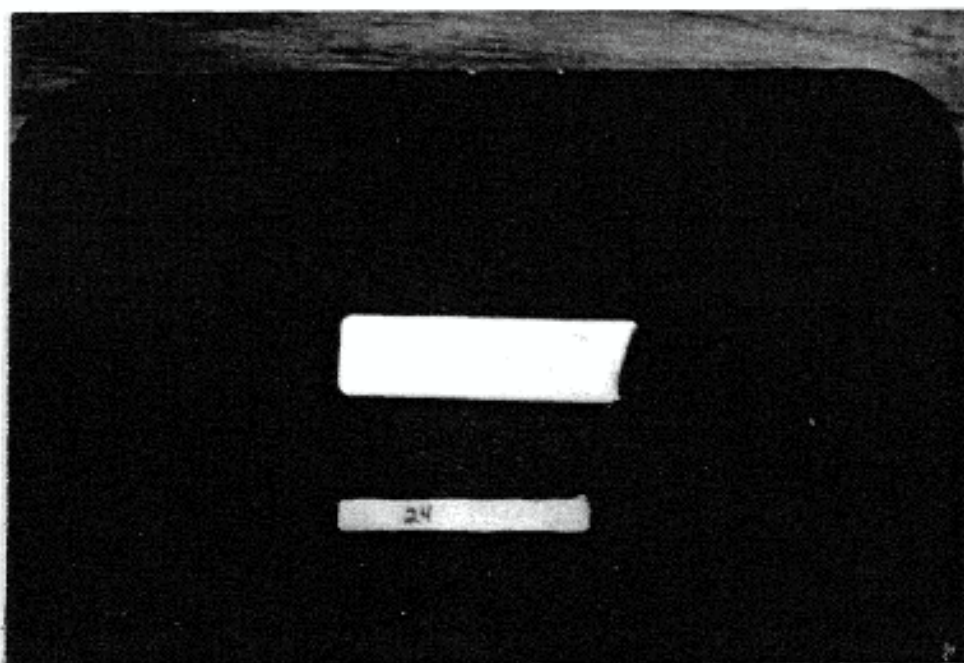
Figure 4. Freeformed (bottom) and a cast (top) Nylon 6 bar specimen . Scale 0.3"=1.0"

## TABLE IV TENSILE TEST DATA FOR EFF/CAST NYLON 6 SPECIMENS

| Specimen | Yield Stress (MPa) | Young's Modulus (MPa) | % Elongation at Break |
|---|---|---|---|
| Control TMI Cast | 83.02 | 2248 | 3.51 |
| EFF TMI | 74.52 | 2257 | 3.10 |
| Control TMXDI Cast | 74.59 | 2257 | 4.31 |
| Commercial Cast Nylon 6 (Unfilled) | 80 | 3280 | 3.5 |

* Resin compostion 30g caprolactam, 8 wt. % fume silica, 1 mol. % TMI, 2 mol. % Na Caprolactamate

From the results above it can be seen that the extrusion freeformed bars had lower strengths and elongation to break values than those cast under identical conditions. This suggested that the nylon in the extrusion freeformed bars may have a lower molecular weight than that present in the cast bars. It is possible that exposure of nylon resin to the atmosphere during extrusion may have an inhibitory effect upon its polymerization (13). The difference in mechanical properties between the extrusion freeformed bar and both the cast control and commercial specimens was not significant, however.

## TABLE III CAST NYLON 6 TENSILE TESTING RESULTS

| Sample | Yield Stress (MPa) | Young's Modulus (MPa) | % Elongation @ Break |
|---|---|---|---|
| 165-15 | 45.29 | 1856 | 3.5 |
| 165-30 | 43.05 | 1821 | 2.4 |
| 165-45 | 54.08 | 2148 | 2.0 |
| 165-4 | 55.6 | 2340 | 1.5 |
| 165-15 ½ TMXDI, Base | 67.4 | 1866 | 16.0 |

The results from the tensile testing indicated that both yield strength and sample modulus increased with reaction time. A concomitant decreasing trend in elongation to break values was also observed. This data was supported by the DSC results which showed an increasing degree of crystallinity for samples with heated for long time periods. Furthermore, the increase in sample elongation to break observed in the sample polymerized with reduced amounts of activator and base suggests that the Nylon present in this sample has a higher molecular weight than that present in the other samples. This too is supported by the DSC results. These results demonstrated that curing the caprolactam resin for four hours at 165° C produced high strength nylon 6 parts.

## Extrusion Freeforming of Nylon 6 Resin

Extrusion freeforming of the resin was accomplished using an Asymtek Automove Model 402 Fluid Dispenser which had a syringe pump attached to the machine dispensing head. In particular, nylon resin was pumped through at 25 gauge needle heated at 70° C onto an aluminum platen heated at 165° C. Photographs of the Asymtek Fluid Dispenser and its syringe pump nozzle in the process of freeforming nylon resin are presented in Figure 2 and 3 respectively.

Preliminary attempts to accurately freeform the nylon resin onto a platen heated at 165° C were met with some difficulty because the resin was much too fluid at these temperatures and completely wetted the platen surface. Consequently, eight weight percent of hydrophobic, trimethylsilylated fumed silica thickening agent was added to the resin to increase its thixotropy. The resin was also reformulated with TMI rather than TMXDI activator in order to further increase its pot life. Test bars specimens were then extrusion freeformed using the reformulated resin. Shortly after extrusion freeforming, the test bar specimens were cured for an additional four hours in a mineral oil bath heated at 165° C. After curing , the bars were tensile tested and a comparison was made between these specimens and bars cast under identical conditions. A photograph depicting both a freeformed and a cast Nylon 6 bar specimen is shown below. The tensile testing results are depicted in Table IV below.

## Conclusions

In this study, it has been demonstrated that a high molecular weight structural thermoplastic can be freeformed from a reactive monomer. Consequently, the materials processing capability of the extrusion freeforming technique can be extended into the realm of processing high strength engineering nylon 6 thermoplastic. Furthermore, the freeformed materials possess mechanical properties comparable to nylon 6 produced using conventional processing techniques. This demonstrates that freeforming technology has the potential to produce functional prototype parts.

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