

Extrusion freeforming of Nylon 6 materials

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Abstract

A modified Nylon 6 formulation, developed originally for reaction injection moulding, has been used to freeform small parts. Liquid monomer is deposited as a fine stream from computer-controlled writing head and polymerizes on a heated plate as the part is built up. This is the first example of rapid prototyping of a linear polymer by direct polymerization. Nylon was chosen for this work because it attains good mechanical properties at relatively low molecular weights, so limiting the extent of chain propagation necessary. Freeformed bars were made with a strength of 75 MPa and tensile modulus of 2.3 GPa. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Numerous commercial rapid prototyping (RP) processes are capable of fabricating complex-shaped components by the sequential addition of layers of material. 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 layers of raw material upon one another. Stereolithography, the original RP process, produces prototypes from heavily cross-linked, and fragile, photopolymers based on acrylate or epoxy chemistry [1]. Selective laser sintering produces parts by fusing polycarbonate powder but the product is porous and weak [2]. More recently, fused deposition modeling, which deposits lines of liquid thermoplastic, has made the transition from wax parts, through hot melt adhesives to ABS parts, which are tough and almost fully dense [3].

We have been exploring methods to extend the materials processing capabilities of RP technology to tough, strong functional prototypes made from linear engineering thermoplastics by direct polymerization of monomer in layers. This is done with a view to developing a flexible route to the characterization of polymers and blends made by concurrent polymerization and solidification rather than by conventional polymerization followed by processing.

One method of fabricating such polymer prototypes utilizes extrusion freeform fabrication techniques (EFF), sketched in Fig. 1. Parts have been built from a series of precisely deposited slurries of ceramic in liquid cross-linking monomer, which is subsequently thermally polymerized to form a particle-reinforced composite (or ceramic greenbody) [4]. The slurry deposition is typically performed using a syringe pump fitted with a fine bore nozzle that is coupled to a three-axis gantry and is interfaced to CAD-based motion control software. This method has been applied to ceramics, metals, composites, gels and thermoplastics [3].

In most of these systems, the immediate shape control is due to addition of a gelling agent to the fluid to give a toothpaste-like rheology. However, to avoid flow and loss of resolution, it is necessary that the monomer system used to fabricate these parts rapidly polymerizes to a high-molecular weight polymer. For a linear chain growth polymerization, this requires a high rate of propagation. It is also necessary that the monomer polymerizes with minimal shrinkage and a small reaction exotherm, otherwise there may be significant stresses or poor adhesion between the freeformed part layers. The requirements are similar to those for reaction injection moulding [5]. A major advantage of freeforming liquid monomer when compared to a molten engineering thermoplastic feedstock is that the former have lower viscosity (which facilitates accurate dispensing) and do not exhibit many of the viscoelastic

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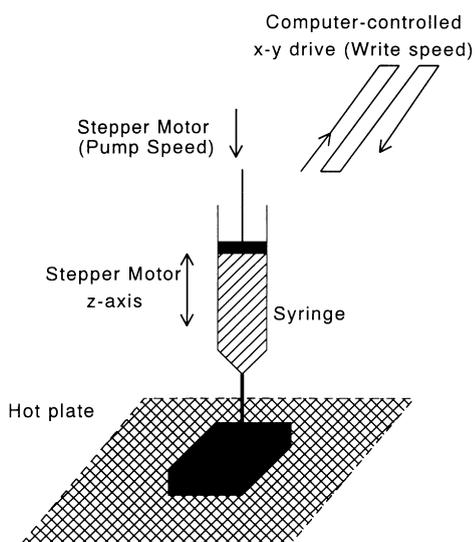


Fig. 1. Sketch of extrusion freeform fabrication equipment.

rheological problems encountered during extrusion of the latter (i.e. die swell) [6].

A review of the literature reveals that caprolactam monomer satisfies the above requirements since it is a low viscosity liquid when molten (70°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 [7]. Caprolactam also has a lower polymerization exotherm than most vinyl monomers and so favours controlled reaction.

Caprolactam can be polymerized by reaction with sodium hydride at 230°C via the mechanism shown in Fig. 2 [8]. The slow initiation step is the formation of an *N*-acylcaprolactam by addition of caprolactamate anion to caprolactam. This then repeatedly adds caprolactamate anion at the ring $>C=O$ to form polymer. Attack on the external carbonyl $>C=O$ is a null reaction. The reaction can be accelerated to run at 150°C by the addition of a cocatalyst such as various *N*-acylcaprolactams or isocyanates which react with caprolactam to form the *N*-carbamoylcaprolactam and then propagate as before.

Rapidly polymerizable caprolactam resin is commercially available in bulk quantities as a two-pack system which is used in nylon casting and reaction injection moulding (RIM) processes [9]. *N*-Carbamoylcaprolactam 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 [10].

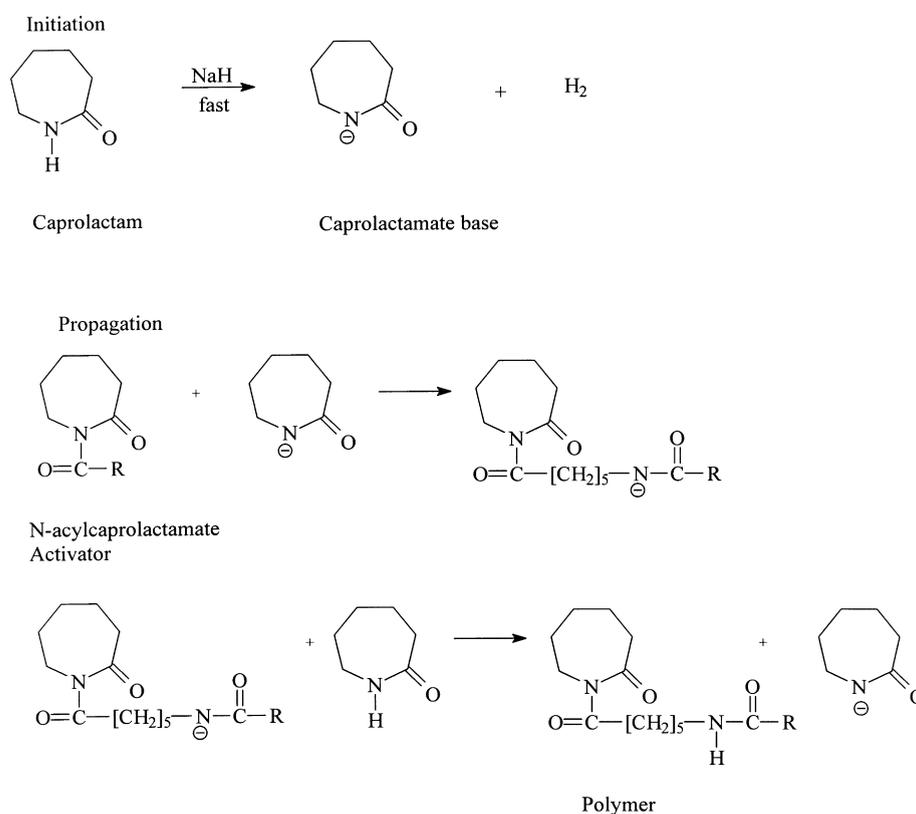


Fig. 2. Anionic caprolactam ring opening polymerization reaction mechanism.

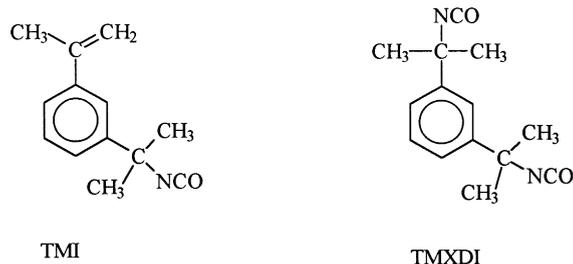


Fig. 3. Tetramethyl-1,3-xylylene diisocyanate (TMXDI) and 3-isopropenyl dimethylbenzylisocyanate (TMI).

2. 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 at 70°C and clog the EFF apparatus syringe pump dispensing system. The gelation reflects the insolubility of Nylon 6 in caprolactam at this temperature. The resin had to be reformulated with an activator that was stable at the EFF pump reservoir temperatures (70°C), while having the ability to polymerize the resin shortly after dispensing onto a resin curing platen heated at 165°C.

Tetramethyl-1,3-xylylene diisocyanate (TMXDI) and 3-isopropenyl dimethylbenzylisocyanate (TMI) were two compounds found to be suitable EFF-compatible latent polymerization activators (Fig. 3). TMXDI gives a cure time of 10 min at 165°C and 35 min at 70°C when used at 1 mol.% (based on isocyanate function) with 2 mol.% of sodium caprolactamate activator. TMI gives a cure time of 20 min at 165°C and 45 min at 70°C at the same concentrations. Ideally, for stable fluid properties during processing combined with rapid solidification, the gel time at 70°C should be longer than a few hours and that at 165°C should be a few minutes, but the activators shown are satisfactory.

Optimal curing conditions for the reformulated resins were determined by measuring the crystallinity and crystallization undercooling on cast Nylon 6 specimens using differential scanning calorimetry (d.s.c.) on cast samples polymerized with 1 mol.% NaH and 1 mol.% TMXDI. For cure times up to 1 h at 165°C, the crystallinity

was around 40% but increased to 50% on annealing for 4 h at 165°C. On reducing the TMXDI content to 0.5 mol.% (based on isocyanate function) the crystallinity was 49% after 15 min cure. Higher crystallinity of these samples was expected to increase the elastic modulus.

The melt undercooling, the difference between the melting point on heating and the crystallization temperature on subsequent cooling at 10°C/min, has been shown to depend on melt viscosity and so on the molecular weight of the Nylon 6 [11,12]. The undercooling increased from 41 to 44°C as the cure time increased from 15 to 45 min at 165°C. Reducing the TMXDI to 0.5 mol.% increased the undercooling to 47°C after 15 min cure, implying a much higher molecular weight.

From the above results it can be seen that the nylon polymer increases in molecular weight and crystallinity upon prolonged reaction and annealing. The melting point of Nylon 6 is 216°C, so much of the reaction must occur in the solid state. The molecular weight of the final nylon polymer was found to level off after a 4-h 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 quasi-living process where polymer product molecular weight is inversely proportional to activator concentration [13]. 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 1.

Both yield strength and sample modulus increased with reaction time. A concomitant decrease in elongation to break was also observed. These changes can be attributed to the increasing crystallinity for samples heated for long time periods. A higher elongation to break was observed in the sample polymerized with reduced amounts of activator and base. This again suggests that this sample has a higher molecular weight.

These results demonstrated that the TMXDI activator gave a resin with a reasonable lifetime at 70°C, rapid gelation at 165°C, and which produced high-strength Nylon 6 parts after 4 h annealing at 165°C.

Table 1
Cast and EFF Nylon 6 tensile testing results (seven samples, range \pm 10%)

Sample	Yield stress (MPa)	Young's modulus (MPa)	% elongation at break
165°C, 15 min	45	1860	3.5
165°C, 30 min	43	1820	2.4
165°C, 45 min	54	2150	2.0
165°C, 4 h	55	2340	1.5
165°C, 15 min (1/2 TMXDI, base)	67	1870	16
EFF TMI	75	2260	3.1
Control TMI cast	83	2250	3.5
Commercial cast Nylon 6 (unfilled)	80	3280	3.5

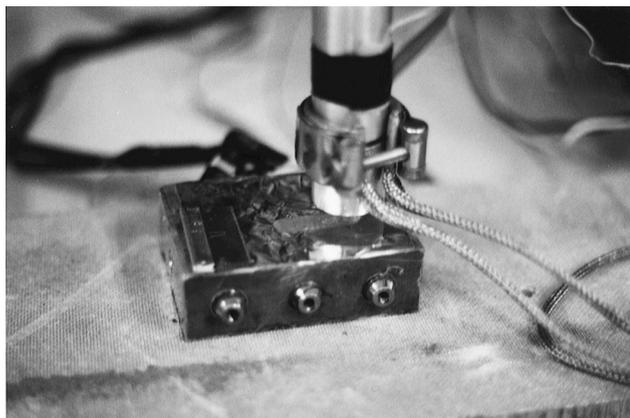


Fig. 4. Photograph of Asymtek EFF apparatus syringe pump nozzle free-forming nylon resin onto a heated aluminum platen.

3. 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. The monomer–catalyst mixture was pumped through a 25-gauge needle heated at 70°C onto an aluminum platen heated at 165°C (Fig. 4).

Initially, the monomer was much too fluid at these temperatures and completely wetted the platen surface. Polymerization was not rapid enough to allow gelation before flow occurred. Consequently, 8 wt.% of hydrophobic, trimethylsilylated, fumed-silica thickening agent was added to the resin to produce a thixotropic gel (Aerosil R504, Degussa Corp.). Careful drying of the silica was necessary in order to avoid deactivation of the catalyst by water.

The resin was also reformulated with TMI rather than TMXDI activator in order to further increase its pot life at 70°C. Test bars specimens were then extrusion freeformed using the reformulated resin (resin composition 30 g caprolactam, 8 wt.% hydrophobic fumed silica, 1 mol.% TMI, 2 mol.% NaH). Shortly after extrusion freeforming, the test bar specimens were cured for an additional 4 h 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. The tensile testing results are depicted in Table 1.

From the results above it can be seen that the extrusion freeformed bars had only slightly lower strengths and elongation to break values than those cast under identical conditions or than commercial Nylon 6.

4. Discussion

No linear polymerization is sufficiently fast to allow cure before the low-molecular weight monomer flows on a hotplate. Hence some form of physical setting must precede polymerization. For most organic liquids, this can be

provided by the addition of hydrophobic silica to produce a gel with a low enough shear strength to permit extrusion, but high enough to sustain the shape of several layers until gelation occurs [3]. The shape change of a depositing thixotropic bead on a substrate has been analysed [14,15]. A bead deforms under surface tension until this is balanced by the shear yield stress of the gel.

In an ideal polymerization reaction for freeform fabrication, the reaction should be essentially complete in a few minutes after delivery of the liquid. This is difficult to achieve because of a number of constraints. The need for a long pot life, at about 100°C below the reaction temperature, requires that the reaction have a high activation energy. Other things being equal, highly activated reactions will tend to be slower at all temperatures.

To form a high-molecular weight polymer in a few minutes, the propagation reaction must be rapid, greater than about 0.1 l/mol·s. Most vinyl polymerizations are in this category but condensation and ring-opening polymerizations tend to be slower. Unlike in RIM processes, the evolved heat of reaction cannot be used to accelerate the process because very non-uniform parts result. Instead, the heat of reaction should be low and thermal conduction should be sufficient to prevent much heating.

In addition, the system should be sufficiently insensitive to oxygen and moisture that inhibition does not occur as a result of diffusion into the thin layers as they are deposited. Alternatively, freeforming may be carried out in a controlled atmosphere.

The answer to these constraints used in stereolithography [1] is to form a highly cross-linked acrylate or epoxy system. Gelation occurs at a low extent of reaction, at which point the shape is defined and full polymerization occurs slowly. However, heavily crosslinked polymers are also brittle. In the Nylon 6 system, gelation occurs early as a result of precipitation. However, the polymer achieves very high toughness at relatively low chain lengths, compared to other linear polymers. Under our conditions the caprolactam polymerization is sufficiently slow that the part reaches only enough strength, through gelation, to support its own weight during the deposition process. In these circumstances the polymerization exotherm is not an issue. It is fortunate that atmospheric water does not deactivate the sodium caprolactamate during the deposition process. Since each 1 mm thick layer is only exposed on the top surface for about 1 min, there is insufficient time for diffusion into the layer.

5. Conclusions

In this study, it has been demonstrated that a high-molecular weight structural thermoplastic can be free-formed 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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