

National Textile Center

FY 2003 (Year 12) Continuing Project Proposal

Project No.

M01-NS03

Competency: Materials

Lewis Acid-Base Complexation of Polyamides and the Effect...

Project Team:

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Objective:

It is generally believed that hydrogen bonding makes polyamides important engineering plastics, because of the high strength it imparts. However, the interchain hydrogen bonds between amide groups are seen as a barrier to ultradrawing of high molecular weight polyamides and, therefore, to the achievement of ultrahigh strength and ultrahigh modulus fibers. The purpose of the proposed research is to develop a new method to spin and draw high strength fibers and films by suppressing the interchain amide group hydrogen bonding. There is evidence in the literature that hydrogen bond suppression can be achieved by iodination, Lewis Acid - Base complexation of polyamides or mixing with polyamide inclusion compounds, and this may provide a way to temporarily eliminate hydrogen bonding during drawing, allowing orientation to the desired degree, followed by reformation of the hydrogen bonds in the oriented state. We will investigate the influence of hydrogen bonding on fiber formation in low and high molecular weight polyamides, and examine morphological characteristics such as molecular orientation in the crystalline and noncrystalline regions, degree of crystallinity and crystallite size. We will also explore the Lewis acid - base complexation reactions of polyamides as a means of probing the nature of intermolecular hydrogen bonding in semicrystalline polymers.

Progress Statement:

The purpose for this year's project was to develop a new method to spin and draw high strength nylon fibers and films by suppressing the interchain amide group hydrogen bonding. We have shown that hydrogen bond suppression can be achieved either by Lewis Acid-Base complexation of polyamides with GaCl₃ or mixing with polyamide inclusion compounds formed with cyclodextrins (CDs).

This provided a way to temporarily eliminate hydrogen bonding during drawing, allowing orientation to the desired degree, followed by reformation of the hydrogen bonds in the oriented state. In the present study, we have drawn PA66 complexed films up to a draw ratio of 40 (Figure 1) and have been able to regenerate PA66 by immersing in water for at least 24 hrs.

The appearance of the complexed films is completely different from as-received PA 66 film. The complexed films are transparent and behaved like rubbery material, while the as-received PA66 film is rigid and opaque. Unlike neat PA66, these complexes are soluble in organic solvents such as nitromethane. It is important to mention that N66-GaCl₃ films are completely amorphous, and handling of these films becomes difficult particularly when the fiber-forming N66 grade is used.

We have used a fiber forming N66 with molecular weight of 16,773 g/mol, and shown that the initial modulus can be increased by 200% when DR was 10 (Figure 2). The films drawn 40 times had a low degree of crystallinity of 25%. We have concluded from these studies that a high molecular weight N66 may be needed.

A great deal of effort was spent to increase the molecular weight of N66 polymer. We have finally demonstrated that a super high molecular weight Nylon 66, with molecular weight up to 170,000 g/mol (Figure 3), can be

produced by solid state polymerization of N66 chips. Higher molecular weight is feasible when the polymerization is carried out under high vacuum. We have shown that a super high molecular weight N66 can be complexed with GaCl₃ in nitromethane. We have produced 2% film forming solutions from N66 (complexed with GaCl₃) having molecular weight of 170,000 g/mol. We are the first to achieve this, and hope these films and fibers have a greater potential for making high modulus and high strength materials.

We have also demonstrated that the extent of hydrogen bonding can be quantified using FTIR and solid state NMR spectroscopy. Morphological characteristics, such as degree of crystallinities and molecular orientation, were characterized using X-ray diffraction (Figure 4), density measurements, DSC, FTIR and solid state NMR.

Nylon 6 has been included as a guest in the narrow channels of the inclusion compound (IC) formed with host α -CD. The nylon 6 sample coalesced from its α -CD-IC crystals showed a nearly two-fold increase in the level of crystallinity. In addition, only the α -form crystalline polymorph was produced by the coalescence process, while the as-received nylon 6 contained both α - and γ -form crystals, as confirmed by solid state ¹³C NMR and FTIR observations. This result seems consistent with the narrower, nearly all-trans α -form crystalline conformation being included preferentially in the α -CD-IC channels compared with broader, non-planar γ -form crystalline conformation. Also the antiparallel packing of nylon 6 chains in the α -form crystals would lead to an anticipated maximum level of crystallinity of ~50% for the coalesced, if nylon 6 chains were included randomly in up and down directions in the α -CD-IC crystalline channels. This is in fact close to the level of crystallinity (~53%) actually observed for the nylon 6 sample coalesced from its α -CD-IC.

Most recently well-mixed blends of nylon 6/nylon 66 have also been achieved by coalescence from their common α -CD-IC. Preliminary DSC observations revealed complete suppression of nylon 6 crystallinity and a broad melting endotherm that encompasses the T_m of nylon 66. These observations indicate substantial molecular mixing of the nylon 6 and nylon 66 chains in the blend coalesced from their α -CD-IC

Next Year's Goals:

Utilize a super high molecular weight Nylon 66 of molecular weight 170,000 g/mol or higher, complex it with GaCl₃ and produce fibers with a high modulus and tenacity. Scale-up of the production of N6/N66 blends obtained by coalescence from their common CD-IC is also high on our agenda, so we may investigate their fiber forming characteristics.

Approach:

As the last phase of this project begins we intend to focus on the research activities which will lead to the development of the technology for making super high strength nylon fibers. Our recent studies have shown that N66-GaCl₃ complexes are stable enough to be processed by melt spinning. We shall use this approach along with the wet spinning technique, which is also available in our department. Scale-up trials shall be conducted at Honeywell.

Solid state CP/MAS/DD NMR is a powerful tool to monitor structure and morphological changes in semicrystalline polymers. Various pulse sequences can be used to characterize crystalline and amorphous phases separately. As we indicated in our annual report we will also carrying out detailed solid state NMR analyses determine the extent of hydrogen bonding in partially decomplexed materials.

Outreach to Industry:

Cooperate with Honeywell a maker of super high modulus Spectra fibers on the development of high modulus/high tenacity fibers based N66-GaCl₃ technology.

New Resources Required: No new resources will be required.



Figure 1. A superb drawability (4000 %) of N66-GaCl₃ film on Instron. The initial film length was 3 cm.

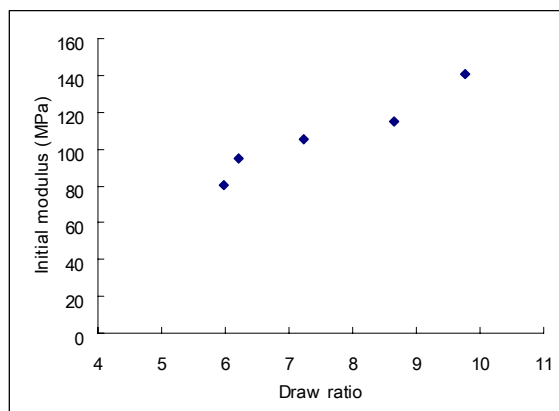


Figure 2. Modulus of regenerated N66 films as a function of a draw ratio

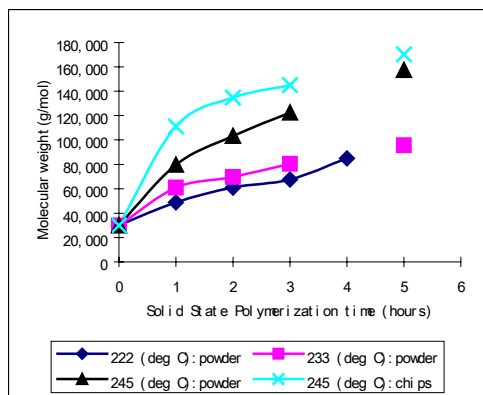


Figure 3. Solid state polymerization of N66

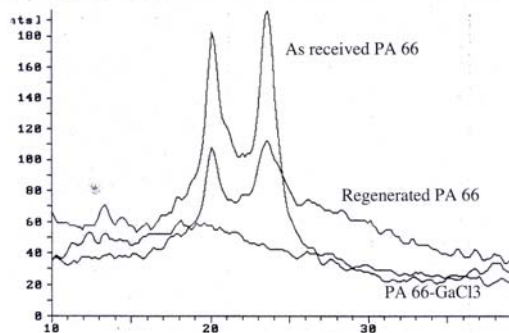


Figure 4. WAXD Pattern of as received PA 66, regenerated PA 66 and PA 66-GaCl₃ complex

Table 1. Thermal Properties Obtained from DSC for as-received and IC Coalesced Nylon 6.

Thermal properties	As-received Nylon 6	Coalesced Nylon 6
T _m (°C)	215.6	219.3
ΔH _f (J/g)	55.8	100.4
Crystallinity (%) [*]	29.4	52.8
T _{cc} (°C)	179.9	180.0
ΔH _{cc} (J/g)	60.2	66.2
Temperature range of crystallization(°C)	190.7-156.8	188.6-161.8

* The ΔH_f of 100% crystalline nylon 6 is taken as 190 J/g.