Transient Confinement of the Quaternary Tetramethylammonium Tetrafluoroborate Salt in Nylon 6,6 Fibres: Structural Developments for High-Performance Properties via a Temporal Weakening of the Hydrogen Bonds

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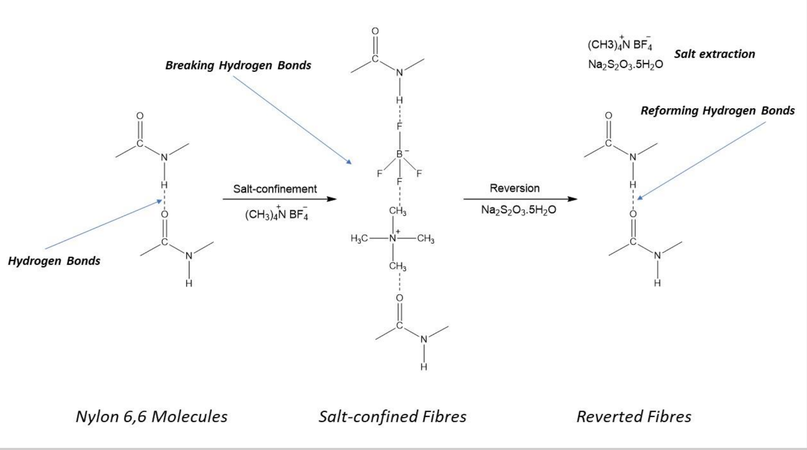
ABSTRACT A temporal confinement of the quaternary tetramethylammonium tetrafluoroborate (TMA BF_4) salt among the polyamide molecules has been used for the preparation of high-modulus and high-strength properties of aliphatic polyamide nylon 6,6 fibres.

In this method, the suppression or the weakening of the hydrogen bonds between the nylon 6,6 segments has been applied during the conventional low-speed melt spinning process. Thereafter, after the complete hot-drawing stage, the quaternary ammonium salt is fully extracted from the drawn 3% wt salt-confined fibres (by using pentahydrate sodium thiosulphate, $Na_2S_2O_3.5H_2O$, solution) and the nascent fibres are, subsequently, thermally stabilized (under tension). The structural developments that are acquired in the confined-nylon 6,6 fibres are ascribed to the developments (improvements) of the overall fibres' properties due to the confinement process. Surprisingly, unlike the neat nylon 6,6 fibres, the XRD patterns of the as-spun salt-confined fibres have shown diminishing of the (110)/(010) diffraction plane that obtained pseudohexagonal-like β' structural phase. Moreover, the β' pseudohexagonal-like to α triclinic phase transitions took-place due to the hot-drawing stage (draw-induced phase transitions). Interestingly, the hot-drawing of the as-spun salt-confined nylon 6,6 fibres achieved the same maximum draw ratio of 5.5 at all of the drawing temperatures of 120, 140 and 160 °C.

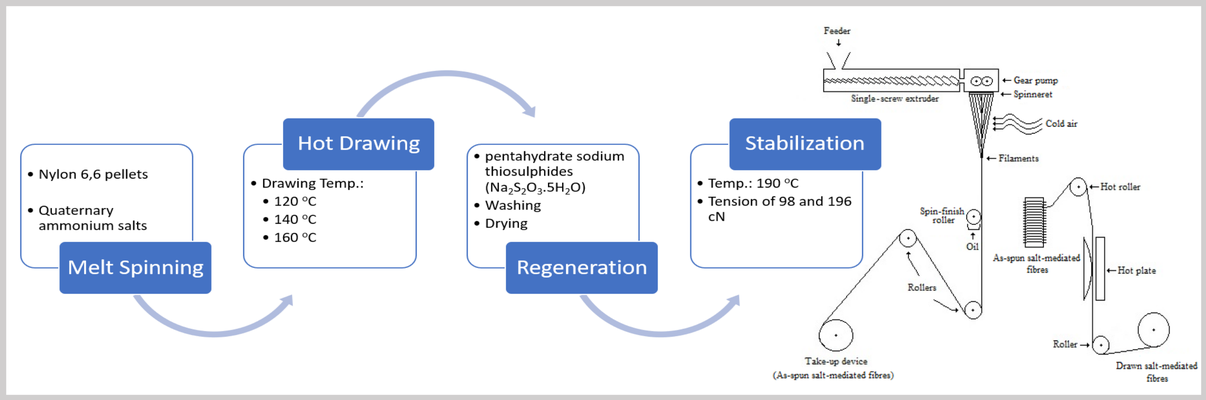
The developments that happened produced improved values of 43.32 cN/dtex for the tensile modulus and 6.99 cN/dtex for the tensile strength of the reverted fibres. The influences of the TMA BF_4 salt on the structural developments of the crystal orientations, on the morphological structures and on the improvements of the tensile properties of the nylon 6,6 fibres have been systematically studied.



INTRODUCTION

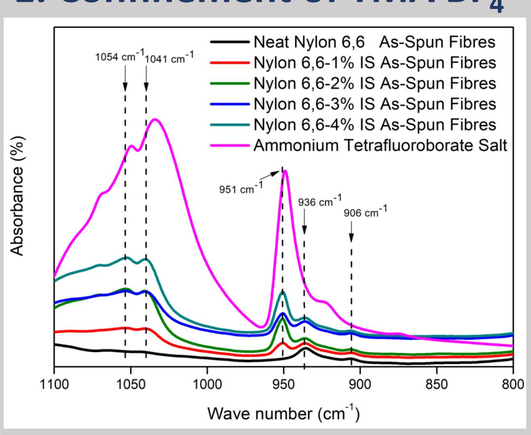
The well-known routes for obtaining high-moduli and high-strength polymeric fibres are the extensibility-based strengthening of the aliphatic molecules as well as the unfoldable-molecules-based stiffening of the aromatic molecules (the stiff molecules do not fold up into lamellae in the presence of aromatic rings). The extensibility-based strengthening arose, theoretically, from having high deformability along the molecular chains of the semicrystalline fibres—such as the flexible ultra-high molecular weight polyethylene. On the other hand, the nature of the crystal structure for extruded nylon 6,6 fibres and films is a pseudohexagonal β crystal phase structure that develops into a triclinic α crystal phase structure. Naturally, the formation of the high-moduli and high-strength nylon 6,6 fibre is, mainly, dependent on the crystalline structure of the as-spun β phases and their development (patently, β to α phases transitions). Here, the hydrogen bonds between the nylon 6,6 molecules are, basically, immobile up to the melting temperature, and these hydrogen bonds constitute the main obstacle towards obtaining the abovementioned high draw ratios and high crystal orientations of the nylon 6,6 fibres. In this research work, novel nylon 6,6 fibres are prepared by the temporal reversible TMA BF_4 salt-confined method using low-speed melt spinning, so as to produce high-strength and high-modulus fibres.

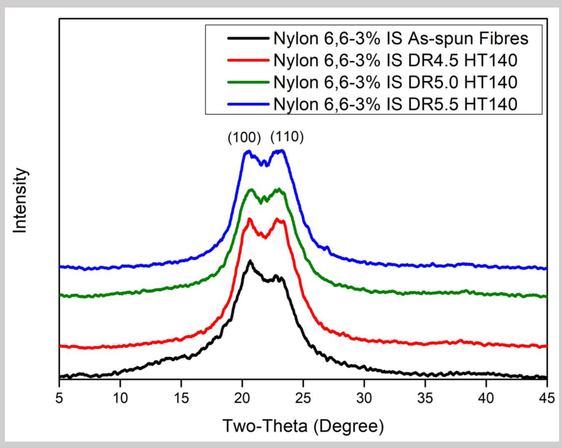
MATERIALS AND METHODS



RESULTS AND DISCUSSION

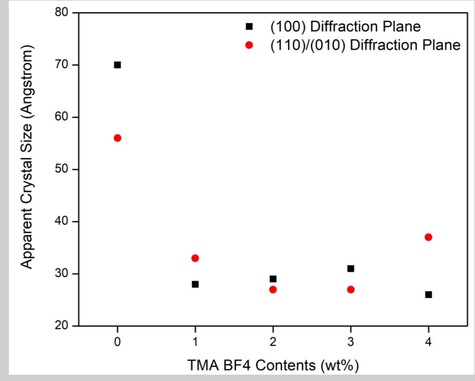
1. Confinement of TMA BF_4





The size of TMA cation of the TMA BF_4 is 0.283 nm – which is smaller than the smallest ionic radius of any other alkylammoniums cations, while the size of the BF_4 anion is 0.229 nm. The nanostructure size of the TMA BF_4 is smaller than the hydrogen bond distance between two adjacent molecules. Therefore, the as-spun salt-confined fibres have exhibited crystal size (ACS) smaller than that of the as-spun neat fibres

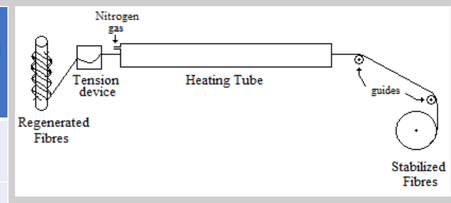
Interestingly, increasing the drawing temperature is found to has no effect on the molecular chain extensibility (draw ratio). This observation suggests that the ammonium salt confinement took place in the amorphous phase.



	Neat Nylon 6,6 Fibres				Salt-confined Nylon 6,6 Fibres			
Drawing Temperature (°C)	Draw Ratio	Tensile Modulus (cN/dtex)	Tensile Strength (cN/dtex)	Elongation (%)	Draw Ratio	Tensile Modulus (cN/dtex)	Tensile Strength (cN/dtex)	Elongation (%)
120	4.0	13.3	2.9	70.9	4.5	19.9	3.1	15.6
120	4.5	13.7	3.1	67.5	5.0	26.5	3.7	14.0
120	5.0	23.3	4.1	29.6	5.5	32.8	5.0	15.1
140	4.0	13.2	3.1	78.8	4.5	20.8	2.8	13.6
140	4.5	16.9	3.3	47.0	5.0	31.8	4.1	12.8
140	5.0	21.8	3.9	33.7	5.5	35.8	4.2	11.6
160	4.5	16.5	3.7	67.7	4.5	27.3	3.1	11.1
160	5.0	20.8	4.0	41.4	5.0	31.0	3.7	11.9
160	5.5	26.3	4.7	30.7	5.5	33.4	4.5	13.5

2. The extraction of the salt and the structural stabilization processes

Fibre Type*	Drawing temp. (°C)	Tension (gram force)	Tensile Modulus (cN/dtex)	Tensile Strength (cN/dtex)	Elongation (%)
Regenerated Nylon 6,6 Fibres -1#	RT	-	35.62	6.31	26.57
Stabilized Nylon 6,6 Fibres 1-1	190	98 cN	39.94	6.81	26.07
Stabilized Nylon 6,6 Fibres 1-2	190	196 cN	43.32	6.99	25.06
Regenerated Nylon 6,6 Fibres -2#	RT	-	39.81	6.48	31.70
Stabilized Nylon 6,6 Fibres 2-1	190	98 cN	33.44	6.55	29.23
Stabilized Nylon 6,6 Fibres 2-2	190	196 cN	35.96	6.94	29.20



The reversion of the salt-confined nylon 6,6 fibres to the pure nylon 6,6 fibres is carried by extracting out the TMA BF_4 and applying thermal processes to the resulting fibres - which is the main aim of this piece of research.

Herein, the (110/010) peak corresponds to the direction of the hydrogen bonding interchain/interasheet. Thus, the reforming of the hydrogen bonding took place among the neighbouring of the extended molecules for the fibres reverted from the drawn 3 wt.% salt confined nylon 6,6 fibres drawn at the drawing ratio of 5.5 at drawing temperatures of 120, 140 and 160 °C.

CONCLUSIONS

- In this piece of research, a temporal (reversible) confinement of the by quaternary tetramethylammonium tetrafluoroborate (TMA BF_4) among the amide groups along the molecular chain is employed to inhibit (or to weaken) the amide (original) hydrogen bonds and forming strong (new) hydrogen bonds between the TMA BF_4 salt and the amide groups (C=O and N-H).
- The XRD patterns obtained pseudohexagonal-like β' structural phase for the (110)/(010) diffraction plane of the as-spun salt-confined fibres that have been hot-drawn to orient the molecules along the fibres' axis draw-induced phase transitions (i.e., β'-to-α phase transitions took-place during the hot drawing stage). This leads to the formation of relatively high-strength and high-modulus fibres.
- The salt-confined nylon 6,6 fibres achieved ultimate molecular orientations of 5.5 at all of the (used) drawing temperatures and also, exhibited crystal size (ACS) smaller than that of the neat fibres under the same conditions which have been developed during the drawing process.
- These improvements are reflected in the achievements of the reverted fibres of an improved tensile modulus of 43.32 cN/dtex and an improved tensile strength of 6.99 cN/dtex (these values can be more improved if a way is found to prevent voids formations inside the fibres).

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