Effects of Clay in Nylon Fiber

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Abstract. Since the introduction of nylon 6:6, and nylon 6, the nylon fiber was in significant demand in home textile and technical textile articles. Its uses in hosiery, sail cloth, parachute, blouses, gowns and veils, swim suit, parachute, and lingerie etc. Improving the performance of any nylon matrix with the loading of clay content, for the desired effects, can be an important subject to expand the utilization of nylon in automotive, technical textiles etc. This review study is to find out how clay may contribute in the performance of nylon fiber, and what research directions are appealing in achieving the desired effects in nylon fibers. The known effects on orientation and crystal structure of any nylon polymer; and how the advantageous effects in the utilization of nylon are achievable through the incorporation of clay mineral particularly in composite fiber. Strength, fatigue and thermal stability are some improved effects possible. Heat resistance and flame retardancy are particularly discussed. The aim of this review study is to realize how the nylon fiber was modified using the montmorillonite clay; and to explore what are the possible effects, and improvement achieved.

1. Introduction
The natural fiber attributes were known to be limited in meeting the variety of requirements for apparel and home textiles. Therefore, the introduction of nylon fiber in industry was perceived as milestone achievement in textile world.

Presently, important applications of nylon fibers are observed in products including sport apparel, travel accessories, fabric, finishing net, sports and adventure equipment etc (1). Market research reports are forecasting strong growth in the future consumption of nylon fiber. An example is a recent report, produced by the Market and Research in 2019, on the future global market of nylon fiber. This report demonstrated the growth opportunities for the key producers in time period 2019-2025 relative to the previous five years (2). Another report has shown the growth rate in the global consumption of nylon fiber at CAGR of 4.6% based on value, i.e., from 2020 to reach USD 58.91 billion by 2028 (3). Therefore, the value addition in the performance of nylon fiber, through nylon-clay composite development, would be advantageous. Technically, nylon is a generic name.

The importance of nylon fiber is indicated as one of the five basic textile developments, in four thousand years, determined by Fortune Magazine in 1940. Nylon fiber was included in five basic textile developments; the remaining four were the mercerization of cotton, synthetic dyes, rayon fibers and mechanical textile manufacturing. The five basic textile developments with one more important development, wetting agent, were the landmark achievements. Nylon was the first synthetic fiber manufactured in USA (4).

Nylon was first synthesized as nylon 6:6 by Wallace Hume Carothers (DuPont. Subsequently, nylon 6, nylon 66, and nylon copolymers were developed by IG Farben for applications in plastics (5). The American Chemical Society appreciated landmark contribution of Seaford, Delaware, Plant by designating it as the National Historic Chemical Landmark (6).
However, nylon fiber production in China is based on nylon 6; the expensive nylon 66 resin and nylon 66 fibers are not produced or imported in China. North America and Europe were the main consumers for the nylon staple fiber and bulk continuous fibers utilized in carpet manufacturing (7).

Presently, fine denier, soft and smooth feel, strength and lasting texture enable nylon-6 fiber in variety of apparel clothing, particularly in women intimate garment. The various types of nylon fiber are possible (8) in terms of the polymer matrix (Figure 1).

![Figure 1. Types of nylon fibers known in the market with nylon-6 as the main fiber used](image)

The aim of this review study is to realize how the nylon fiber was modified using the montmorillonite clay and to explore what are the possible effects, and improvement achieved in nylon through the incorporation of montmorillonite clay content. This subject concern will guide the important research areas for further studies in nylon- montmorillonite composite fiber.

Clay mineral particularly montmorillonite are available in nature and exhibited variety of useful effects when used as filler or additive (9-10). It is known to impart interesting effects to textile fibers including heat resistance, flame retardancy, strength, water absorbency, polymer matrix etc. (11-13), and antimicrobial activity coupled with hydrophobicity (14).

### 2. Clay Mineral in Nylon-6

A variety of polymers are receiving interest these days for performance enhancement through the dispersive mixing of clay mineral. Review study on clay/ polymer composites, in 2004 by Gao, indicated the commencement of clay/ polymer nanotechnology with the Toyota’s research studies on clay exfoliation in nylon 6 (15). Moreover, the use of nylon 6/ clay nanocomposite in producing timing belt cover for Toyota Cars was the beginning of commercial application of polymer/ clay nanocomposite.

Studies spreading over twenty years (1985-2005) showed milestone achievements in the development of polymer- clay nanocomposite (Table 1) (16). Nylon- clay hybrid (NCH) structure is receiving research interest since 1980’s.

| S.No | Year | Achievement                                                                 | Polymer-clay hybrid type or effect                      |
|------|------|------------------------------------------------------------------------------|--------------------------------------------------------|
| 1    | 1985 | First polymer/ clay hybrid composite was introduced.                         | Nylon 6- clay hybrid (NCH)                             |
| 2    | 1989 | Car equipped with polymer- clay hybrid component was launched                | Car component were based on NCH                        |
| 3    | 1997 | Gilman found flame retardancy in polymer- clay nanocomposite (PCN)           | Flame retardant NCH                                    |
| 4    | 1997 | Polypropylene- clay nanocomposite                                             | Compatibilizer was used in polymer- clay nanocomposite |
| 5    | 1998 | Compounding method for PCN                                                   | Compounding                                            |
| 6    | 2002 | Invention of nanocomposite hydrogel by Haraguchi.                            | Nanocomposite hydrogel                                 |
The nylon/clay hybrid (NCH) is investigated for the crystal structure and the formation of α-crystal γ-crystal formation. The NCH product performance effects are evaluated or discussed for the possible utilization in automotive parts, and composite filament or fiber sector (Figure 2).

| Studies in clay loading in nylon 6/nylon 6:6 |
|---------------------------------------------|
| Effects on nylon crystal structure |
| Effects on desired performance properties |

| Selection of process |
|----------------------|
| Nylon/clay hybrid |
| Product formation (cord, filament, fiber etc.) |

| Evaluation of the effects |
|---------------------------|
| α-crystal and γ-crystal formation |
| Tenacity, Young modulus, fatigue |

**Figure 2.** Studies in the effects of clay loading to any nylon matrix

### 3. Thermal Stability in Nylon Fiber

#### 3.1. Inherent Thermal Stability in Nylon Fiber

The available research literature in the utilization of clay mineral mainly investigates the incorporation of clay layers in the nylon polymer structure without altering the nylon chemical structure. Any flame retardant or heat resistant effect obtained was then compared with the native nylon polymer. The location of clay layers in nylon polymer influences the heat transmission path and the physical properties, particularly the strength, abrasion, and thermal stability.

Use of clay mineral for improving the flame retardant and heat resistant effects in any nylon fiber may possibly be in any of the following areas:

I. Enhancing the flame retardant or heat resistant temperature performance for specified textile article, and fiber structure.

II. Improving the heat resistant aging effect (i.e. prolonged exposure to elevated temperature) without losing to the useful properties).

III. Providing resistance to chemical solvent degradation at given temperature, particularly to concentrated acids, phenols, and bleaching agents.

IV. Study of relative flame retardant effects in various types/grades of nylon fibers.

The assessment of a material flammability in terms of char length, burning rate, ignition time, heat of combustion, thermal decomposition temperature are useful. Relating the nylon-6/ clay composite flammability to clay dispersion (exfoliation or intercalation), the studies to date in nylon-6/ clay hybrid structure, are significantly lacking to address these areas.

#### 3.2. Heat Resistant Effect in Nylon- 6

The influence of heat in the molecular structure of nylon 6- clay hybrid (NCH), was observed to be reduced relative to nylon-6 alone. The dynamic viscoelasticity study with temperature showed smaller heat absorption in the amorphous phase of nylon- 6 in presence of montmorillonite layers. Increasing the thermal stability without losing the fiber strength properties are desirable in application. This is an interesting research area in producing the nylon-6/ montmorillonite composite fiber. Analysis through XRD, and TEM of melt- intercalated NCH composite demonstrated strong interaction between nylon-6 molecules and montmorillonite layers (17). Possibly an earliest effect of montmorillonite on nylon-6 determined for heat resistant performance, was the heat distortion temperature.

#### 3.3. Flame Retardancy in NCH

Particular interest in the study of flame retardancy of NCH is not significant in literature. Since the intercalation and exfoliation of silicate layers in nylon matrix is known for an increased heat distortion
temperature. The montmorillonite layer of 10 Å thick when intercalated in nylon-6, the repeat unit of nylon-6 matrix increased 12Å to 21Å. The heat distortion temperature observed 65 °C in nylon-6 enhanced to 152 °C in NCH with 4 wt. % loading of montmorillonite (18).

Higher level of layer separation in montmorillonite is obtained in exfoliation. Exfoliated or delaminated montmorillonite layers are obtained when polymer matrix separates the layers by 80-100 Å (19).

4. Other Effects in Nylon-clay Hybrid

Interestingly, twin-screw extrusion may produce NCH with properties comparable to in-situ polymerization. There are other methods in development to produce polymer-clay hybrid including solid intercalation, convulcanization and sol-gen method (15).

Fiber and filament can be produced from NCH. However, a number of research subject areas are there for significant research studies in the future work including:
   a. How the montmorillonite layers are dispersed in nylon matrix; and
   b. Relating the desired enhancement effects produced in NCH composite with the dispersion of montmorillonite and amount of loading.

4.1. Nylon-6 Crystallite and Nylon 6-clay Hybrid (NCH)

How the nylon polymer structure is affected in NCH, and how the desired effects in NCH are obtainable are important subjects to understand.

The level of orientation of nylon-6 crystallites enhances with the montmorillonite loading (20). The orientation of montmorillonite and nylon-6 crystallites in NCH film was assessed using XRD (X-ray diffraction) and TEM (transmission electron microscopy). The dispersion of montmorillonite layers in nylon-6 matrix was observed to produce an increased crystallite size in NCH relative to nylon-6 matrix alone (21).

4.2. Crystal Structure in NCH and Nylon-6 Spun Fiber

The polymer matrix of nylon-6 fibers filled with the montmorillonite exhibited α- and γ- crystals, however, drawing of fiber resulted in α- crystal form only. The improved thermal stability of montmorillonite filled drawn nylon-6 fibers was attributed to the nylon-6 matrix sharing between montmorillonite platelets and hydrogen bonded sheets (22).

The rise in spin-line stress may break the fiber. However, increasing the melt temperature, from 230 °C to 250 °C prevents the fiber breakage (23).

The variation in the tenacity at low take up velocity and high take up velocity was related with the molecular crystallization. Whereas, the stiffness in inter-crystalline regions, caused by the clay content, in nylon-6/clay hybrid fiber resulted in an increased modulus (24).

The results obtained in XRD data indicated α- crystal form prevalent in nylon-6 fiber, and the γ-crystal form in NCH fiber following the annealing and drawing (25).

XRD results showed the rise in α- crystal content with the reduction in γ- crystal in the composite spun fiber at an increased draw ratio. At the clay loading of 0.5 wt. %and an optimum drawing temperature of 120 °C, the maximum values of ultimate tenacity and crystal orientation were achieved (26).

Nylon-6 polymer matrix was sheared in montmorillonite platelet space through hydrogen bonding. The resulting nylon-6/montmorillonite nanocomposite drawn fiber has an increased thermal stability (27).

5. NCH Technical Material

The NCH cords were highly effective in enhancing the cord to rubber adhesion strength (34-55 %) and significant tensile strength improvement (7-21 %) compared to nylon-6 cords (Figure 3). The inferior performance, relative to nylon-6 cords, was shown in fatigue resistance by the NCH cords (28).
Figure 3. Material development using nylon/clay composite

Nylon-6/clay hybrid is the subject of research interest since 1980’s (29). The trend dominating in the research study of nylon-6/clay hybrid was principally for the design and development of polymer, plastic or rubber components for car usage. The earliest research study is claimed by Toyota Company.

There is tremendous room for further research studies in NCH for heat resistant effects; and flame retardant effects in NCH fiber and filament. Fewer studies have considered temperature resistance evaluation following the montmorillonite exfoliation in nylon-6. The properties including tensile, modulus, fatigue, crystallization, impact and creep were determined using the clay as filler in nylon-6.

6. Variety of Clay in NCH Study
All the composite filaments produced from nylon-6/clay hybrid showed significant enhancement in the creep resistance ranging over 10-19 % relative to nylon-6 filament. The NCH composite filament converted into cords and evaluated for the required cord properties including tensile strength, rubber to cord adhesion and fatigue resistance.

However, such composite fiber requires further study to achieve improved tensile strength that was not achievable in the aforesaid referred study (30).

7. NCH Based on Nylon 66
Large number of studies addressing the subject of nylon/clay hybrid; are based on nylon-6 with slight concern to investigate the heat resistance and flame retardancy. Few studies are based on nylon-66/clay hybrid.

Nylon 66 is more thermally stable relative to nylon 6, however, it was less popular possibly for an increased production cost. Therefore, there seems little research interest in the study of nylon 66/clay composite.

Similar improved effects in flame retardancy, Young modulus and strength properties were observed in nylon-66/clay nanocomposite produced using the melt-compounding twin extruder (31).

8. Morphology of NCH
There is not much work undertaken to understand the morphology of NCH, or designing a theoretical model to fully describe the performance of NCH. Truly, the morphology of nanocomposite is a tedious aspect since the quantitative determination of various shapes and sizes of nanoparticle filler is difficult. A useful property is aspect ratio of nanoparticle used. Aspect ratio of nanocomposite can be determined using experimental procedures (32).

An attempt of assessing NCH structure may be possible through using the theories of Halpin-Tsai, and Mori-Tanaka. These theories were applied for the understanding of stiffness of nylon-6 reinforced with LAS; and glass fibers. Moreover, the strength and modulus were enhanced with the increase in the percent loading of montmorillonite in NCH (33).

9. Conclusion
This study finds out and discussed the known effects on crystal structure of any nylon polymer, and how the advantageous effects, and enhancement in the utilization of nylon are achievable through the incorporation of clay mineral in composite fiber. Strength, fatigue and thermal stability, in addition to
crystallization, are some improved effects possible in any nylon matrix. Heat resistance and flame retardancy require further research interest.

The available research literature in the utilization of clay mineral mainly investigates the incorporation of clay layers in the nylon polymer structure without altering the nylon chemical structure. Heat resistant effect is reported in some studies when clay mineral is dispersed in nylon matrix. The particular interest in the study of flame retardancy of NCH is not significant in literature. Therefore, improving the flame retardancy of filament, fiber or fabric, and apparel articles, made of NCH, requires research studies.

10. Conflicts of Interest
The author declares no conflict of interest.

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