

Nylon 6/Clay Nanocomposite Filaments and Their Cords

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ABSTRACT: The present study focuses on the preparation and characterization of nylon 6/clay nanocomposite filaments and their cords. Two different organo modified clays: the ditallodimethyl ammonium salt with bentonite clay (Claytone HY), a commercially available clay from M/S Southern Clay products, USA and silane modified montmorillonite clay (Silane-MMT), synthesized in the laboratory were used to prepare nylon 6/clay nanocomposite filaments. The nanocomposite filaments were tested for tensile and creep properties and compared with nylon 6/sodium montmorillonite (Na-MMT) nanocomposite filaments as well as neat nylon 6 filaments. The clay dispersion within the nanocomposite filaments was analyzed by using X-ray diffraction (XRD), scanning electron (SEM), and transmission electron microscopy (TEM). The creep resistant property of all the nanocomposite filaments showed 10–19% improvement over the neat nylon fila-

ment. However, there is a marginal improvement in tenacity in case of nylon 6/silane MMT nanocomposite filament as compared to the neat nylon filament. All the nylon 6/clay nanocomposite filaments were converted into the cords and tested for various tire cord related properties such as tensile strength, rubber to cord adhesion, and fatigue resistance. The nanocomposite cords showed a significant improvement in tensile property (7–21%) as well as cord to rubber adhesion strength (34–55%) over the neat nylon cords, however, the fatigue resistance was inferior in case of nanocomposite cords. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: E224–E234, 2012

Key words: nanocomposite; nylon 6/clay nanocomposite filaments; tire cord; H adhesion strength; tensile property; creep

INTRODUCTION

Nylon 6/clay nanocomposites have been extensively investigated in the past few years due to their improved thermal,^{1–3} mechanical,^{4–6} and gas barrier properties.^{7–9} These Nylon 6/montmorillonite (MMT) nanocomposites based on organically modified MMT clays have been mostly prepared through melt compounding and *in situ* polymerization methods.^{10–13} Although most of the studies based on nylon/clay nanocomposites are in film or molded sheet form, there are fewer studies of their being produced into fiber/filament form.^{14–16} These nylon 6/clay nanocomposite filaments show improved tensile modulus, thermal resistance, and dyeability properties.^{17,18} The structure formation in melt spun thermoplastic fibers is generally affected by the take up velocity, post spinning operations, and the molecular weight of the polymer.¹⁴ The properties of the nanocomposite filaments are additionally dependent on the

other technological parameters like the method of nanocomposite synthesis and nanoclay loading besides the take up velocity and post spinning operations.¹⁵

Textile filaments and cords are used as rubber reinforcement in a variety of products such as tires, belts, hoses, and diaphragms etc.¹⁹ These reinforcing elements carry a major share of the structural load especially in case of automobile tires. For a better service life of a tire, the reinforcing material should exhibit excellent tensile strength and modulus properties, fatigue resistance, cord-tire adhesion level, and dimensional stability. The interfacial adhesion strength between the cord and the rubber matrix is one of the major determinants of the performance characteristics of an automobile tire. Nylon 6 is the most preferred material for tire cord applications due to its light weight, high elastic recovery, high strength, and toughness. However, the major limitations of nylon tire cords are flat spotting and thermal ageing due to their lower thermal stability and flex fatigue resistance. In addition to that, Nylon 6 tire cord shows poor adhesion to the non polar rubber matrix. Therefore, to improve the cord to rubber adhesion property, the nylon tire cords are coated with resorcinol formaldehyde latex (RFL).²⁰

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It is expected that the addition of clay in the nylon filament and cords can alleviate some of these limitations of neat nylon cords for various applications. Therefore, the aim of this study is to prepare different nylon 6/clay-based nanocomposite filaments, convert them into the cord and investigate the various performance properties. One of the drawbacks of the unmodified Na-montmorillonite (Na-MMT) is its incompatibility with the nylon matrix due to its hydrophilic nature which leads to its agglomeration within the polymer matrix. The modification of clay with an organic compound generally improves its compatibility with the polymer matrix. Such organic compounds are referred to as organomodifiers and the modified clay is referred to as organoclay. Most of the organic modifiers used for nylon/clay nanocomposites as reported in the literature are quaternary ammonium salts and silane coupling agents.²¹ The choice of the modifier depends on its chemistry, thermal stability at the processing temperature, and the "d" spacing between the basal planes of the MMT crystallite structure. The quaternary ammonium salts are the most used compounds to prepare organic clay because they are easily exchanged with the interlayer cations (Na^+ , K^+ , etc.) present in the clay galleries. The quaternary ammonium ion increases the interlayer *d* spacing in the range of 10–20 Å and thus reduces the interlayer attraction which allows the favorable diffusion and accommodation of polymer chains.²² The silane coupling agents are silicon based chemicals that contain both inorganic and organic reactivity in the same molecule. The general formula of silane coupling agent is $(\text{RO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{X}$, where RO is hydrolysable group, which gets converted to silanol group on hydrolysis and X is the organofunctional group. The most important property of silane coupling agent is that it can act as an interface between the clay and the polymer and thus enhances the bond strength as well as prevents the debonding at the interface during composite ageing and use.²³ Most of the reports on nylon 6/clay nanocomposite filaments are based on the use of Closite 30B (quaternary ammonium salt with MMT),¹⁸ aminolauric acid modified MMT,¹⁷ 1,2-aminododecanoic acid modified MMT,¹⁴ and dimethyl dioctadecyl quaternary ammonium modified MMT clays.²⁴

In the present study, two different clays (a) ditallo dimethyl ammonium salt with bentonite, commercially available as Claytone HY from M/s Southern Clay products, USA and (b) γ -aminopropyltriethoxy silane modified MMT clay prepared in the laboratory have been used to prepare nylon 6/clay nanocomposite. The different Nylon 6/clay nanocomposite filaments were produced using the melt intercalation route. The mechanical and creep properties of these filaments were investigated. Finally

the produced nanocomposite filaments were converted into the cords and the important properties of the cords such as tensile strength, creep, adhesion etc were studied and compared vis-a-vis neat nylon cords.

MATERIALS AND METHODS

Materials

Nylon 6 chips (cord grade, Melting point: 224°C) were kindly supplied by M/s SRF Limited, Chennai, India. The clays, Sodium Montmorillonite (Na-MMT) and Claytone HY (ditallo dimethyl ammonium salt modified bentonite clay) were procured from Southern Clay Products USA. γ -aminopropyltriethoxy silane (Silane coupling agent) was procured from Dow Chemicals USA. Reagent grade acetone (Merck) was used as a solvent. RFL solution used was supplied by M/s J K Tire Plant at Kankarli, Rajasthan, India.

Methods

Modification of clay by silane coupling agent

The Na-MMT clay (3 wt %) was dispersed in deionized water (100 mL) at 65°C to form a slurry. The clay slurry was acidified with an organic acid at pH 4–5. γ -aminopropyltriethoxy silane (2 wt % of clay) was added drop wise into the clay slurry with continuous stirring and the mixture was kept at 65°C for 1 h. The silane modified montmorillonite (Silane-MMT) clay was washed, filtered and dried at 65°C. The dried Silane-MMT was ball milled at 200 rpm for 30 min to convert it into a free flowing powder. The average particle size of the clay was 500 nm as determined from Particle Size Analyzer (BECKMAN COULTER Delsa Nano C DLS)

Characterization of clay

Thermogravimetric analysis of different clays was carried out on Perkin-Elmer TGA-7 system (MA). The thermograms were obtained under nitrogen atmosphere at a uniform heating rate of 10°C min⁻¹ in the temperature range 60–780°C. X-ray diffraction (XRD) pattern of the clay powder was recorded in the 2 θ range of 1.5°–40° on X-Pert Scanning ProPana analytical X-ray diffractometer from Phillips (Almelo, Netherlands). Cu K α radiation with a wavelength of 1.54 Å was used for the X-ray diffraction study. The infrared spectra of the clay samples were recorded between 400 and 4500 cm⁻¹ on a Perkin-Elmer Spectrum-BX FTIR system (MA) using KBr pellet technique. The KBr pellets were prepared by grounding one part of the sample with nine parts of spectral

grade KBr and pressed in an evacuated die under suitable pressure to get pellets.

Preparation of nylon and nylon clay nanocomposite filaments

The nylon and nylon clay nanocomposite filaments were prepared by using melt intercalation route. The different clays used Na-MMT (1% w/v), Silane-MMT (1% w/v), and Claytone HY (1% w/v) were dispersed in acetone and ultrasonicated for 10 min. The nylon chips were added in the clay dispersion and sonicated for 30 min. The physically mixed nylon clay chips were oven dried at 65°C and vacuum dried at 80°C for over night.

Nylon and nylon clay nanocomposite filaments were spun on a laboratory scale DSM 5 Micro Twin Screw Compounder, Netherland, attached to a fiber winding device, under optimized spinning conditions i.e., temperature 240°C, screw speed at mixing 200 rpm, residence time 2 min and screw speed at spinning 10 rpm. The spinning was carried out under nitrogen atmosphere.

The extruded filaments were drawn on a laboratory drawing machine with a two-stage drawing process at 65 and 115°C, respectively. All the filaments were fully drawn (draw ratio varying from 4–6), that is, to an extent, beyond which the filaments turned white on further drawing. The final fineness of the filaments was in the range of 5.3–6.3 Tex.

Characterization of filaments

The surface morphology of nylon and nylon clay nanocomposite filament was studied using ZEISS EVO 50, SEM Germany. The filament surface was etched by spraying 15% concentrated formic acid before being observed under scanning electron microscope to see the proper distribution of the clay in nylon matrix.

The dispersion of the clay with in the nylon matrix was studied using Phillips C M 12 transmission electron microscope (TEM), Netherlands. The fine filament cross section was cut using ultra microtome (Lieca EM UC 6). The fine cross section was transferred over the carbon grid and examined under the transmission electron microscope.

X-ray diffraction (XRD) pattern of the nylon and nanocomposite filaments was recorded in the 2 θ range of 1.5°–40° on X-Pert Scanning ProPanalytical X-ray diffractometer (Almelo, Netherlands) from Phillips. Cu K α radiation with a wavelength of 1.54 Å was used for the X-ray diffraction study.

Preparation of nylon and nylon clay nanocomposite cords

The nylon and nylon clay nanocomposite filaments were converted into a cord using 24 monofilaments

with four twist per inch in Z direction on a two for one twister machine. The fineness of the cords was in the range of 145.4–147.4 Tex.

Mechanical properties of nylon and nylon clay composite filaments and cords

Tensile testing. Tensile testing of the filaments was carried out on an Instron 4301 tester with 1-kg load cell. The gauge length was 100 mm, and the strain rate was kept constant at 300 mm min⁻¹. For cords the load cell used was 100 kg and the gauge length was 150 mm with strain rate of 120 mm min⁻¹. Ten specimens were tested for each sample, and the average value is reported. The coefficient of variation (CV%) for all samples was within 5%.

Creep testing. Nylon and nylon clay nanocomposite filaments were subjected to creep testing to determine their long-term mechanical stability. The filaments (gauge length 25 mm) were subjected to 10% of their breaking load, and the readings were taken at frequent intervals up to 24 h with a cathetometer to determine the creep setting. The creep percentage was calculated as per the following formula.

$$\text{Creep \%} = \left\{ \frac{(\text{Final length of filament} - \text{Initial length of filament})}{\text{Initial length of filament}} \right\} \times 100$$

RFL dipping of nylon and nylon clay nanocomposite cords

Dipping of nylon cords was carried out for 10 s in resorcinol-formaldehyde-latex (RFL) solution. The excess solution was removed in a padding mangle (at 4.5 kg cm⁻² pressure). The dipped cords were dried in an air oven at 200°C for 2 min under stretched condition. The tension applied was 0.1 g/ Tex for all the samples.

H-adhesion test

H Adhesion test is a specially designed test for textile cord structures to measure the adhesion property of reinforcing cords to the rubber compounds. The H adhesion test was carried out for RFL dipped nylon and nylon clay nanocomposite filament cords according to ASTM D 4776 method. In this test, specimen is sandwiched between two rubber test blocks in a form resembling an “H” shape, placed in a heated mold and cured at a specific temperature and pressure. The sandwiched test specimen is then cut to create an H test specimen consisting of a single cord with each end embedded in the center of a tab end of the rubber test block. The H shaped

specimen were tested on Zwick UTM 1445 machine for tensile strength keeping gauge length 18.83 mm and a test speed of 127 mm min^{-1} .

Compression tension fatigue testing

The compression tension fatigue property of the nylon and nylon clay nanocomposite filament cords was measured according to ASTM D6588 method using molded composite specimen in a Goodrich Block Fatigue Tester USA. In this test, the specimen blocks of dimension $5.2 \times 1.2 \times 1.2 \text{ cm}^3$ were prepared by molding the dipped cord in between two rubber layers in a two piece mold at 140°C for 1 h 45 min at 1.5 kg cm^{-2} pressure in a hind hydraulic curing machine. The equipment consists of two rotatable steel discs ~ 6.5 in. in diameter and mounted concentrically 9/1600 apart. One of these discs is mounted on a swivel plate so that it can be skewed with respect to the other. A motor drives the fixed disc. The prepared samples were mounted across the rims of the two discs coupling them together while the discs were in a parallel condition. The swivelled disc was then skewed a given amount and locked in that position. The coupled discs were then rotated by means of the motor drive, causing the rubber block, with impregnated cord, to go through alternate compression and extension cycles, normally at a speed of 1900 rpm. Tests were run to give 10% compression and 10% extension in each cycle. The test was run up to 120-h periods. After the specific time composite blocks were sliced off to remove rubber and then swollen in toluene for 2 days and finally fatigued cords were removed easily by pulling out the cord from swollen rubber blocks. Fatigued cords were dried, conditioned, and then tensile properties were measured and percent retention of properties was calculated.

RESULTS AND DISCUSSION

The mechanical properties of the nylon filament are dependent on its crystalline structure and molecular orientation, whereas the mechanical properties of polymer-clay nanocomposites are highly related to their microstructure which in turn is directly related to the exfoliation and dispersion of clay platelets in the polymer matrix. The dispersion of clay within the nylon matrix plays a key role in determining the mechanical properties of nanocomposite filament. The dispersion of clay platelets in the molten polymer depends on the thermal diffusion of polymer molecules in the galleries and on the mechanical shearing action. Thermal diffusion is favored by modifying the clay surfaces with appropriate organic surfactants, rendering the galleries more compatible with the polymer molecules. Pretreatment of MMT

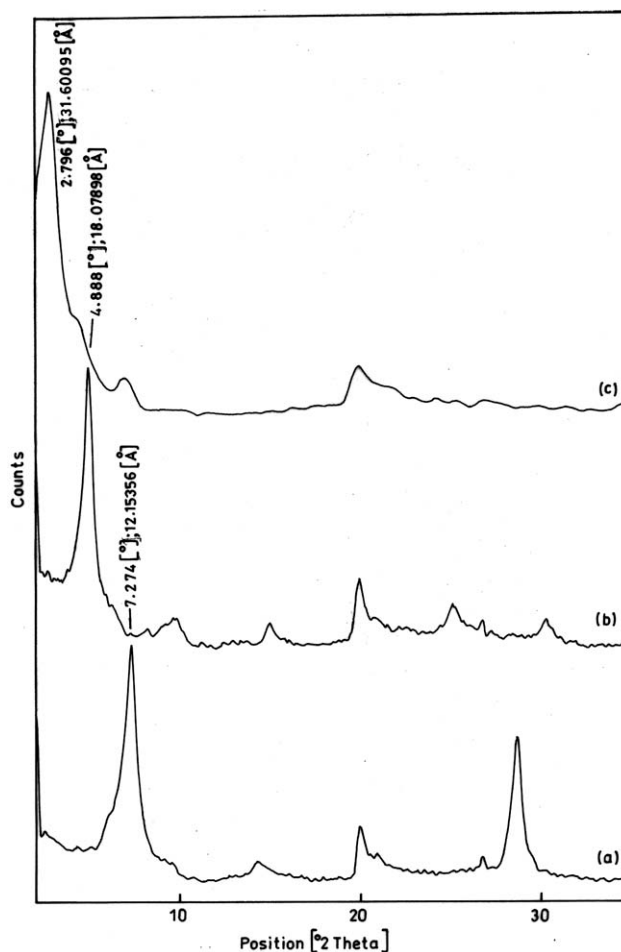


Figure 1 X ray diffractogram of (a) Na-MMT, (b) silane MMT, (c) claytone HY Clay.

is of great importance for the reason that intercalation of macromolecules and polymerization precursors greatly depends on the expanding extent of interlayer distance, surface polarity of silicate layers and compatibility of organic modifier with the polymer matrix.

Clay characterization

The different clays Na-MMT, Claytone HY, and silane MMT were characterized by using wide angle X ray diffraction (WAXD) and Thermogravimetric analysis (TGA) techniques for evaluating the basal spacing, interlamellar structure, and thermal stability, respectively. Figure 1 shows the X-ray patterns of Na-MMT, Clayton HY, and silane- MMT clays.

The X-ray diffractogram of Na-MMT showed the characteristic d spacing of 12.153 \AA at 2θ value of 7.27° . The d spacing of silane-MMT clay is considerably increased as compared to Na-MMT due to the addition of the organic modifier. The silane treated clay exhibits a basal reflection peak (001) at 2θ peak at 4.88° corresponding to interlayer spacing 18.078 \AA . The Claytone HY showed the characteristic

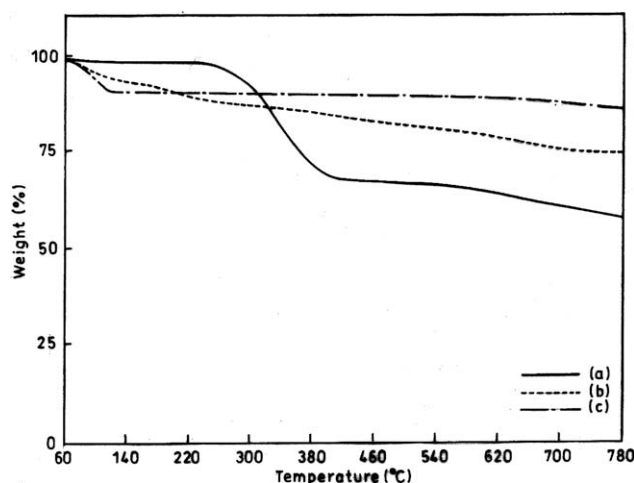


Figure 2 Thermogravimetric analysis of (a) claytone HY, (b) silane-MMT, (c) Na-MMT.

d spacing (001) of 31 Å at 2θ nearly at 2° . The clay Claytone HY is a commercially available ditallodimethyl ammonium salt modified bentonite clay obtained from Southern Clay Products, USA. The unmodified bentonite generally shows the characteristic d spacing (001) of 13.2–15.3 Å at 2θ nearly at 6.7° .^{25,26}

The thermal stability of different clays was analyzed by thermogravimetric analysis technique. The temperature range used for this study was 60–600°C. The TGA thermograms of different clays are shown in Figure 2. It is seen that the Na-MMT clay degrades much less within the test temperature range. The initial minor loss of weight may be due to the removal of moisture. In case of silane-MMT clays a small amount of initial weight loss occurs at near 200°C which may be due to the degradation of residual surface silane. The degradation of Claytone HY starts around 250°C and is maximum at 320°C. Therefore it is expected that the clays would not be thermally degraded to a large extent at melt processing temperature of 240°C, used in this study.

The Fourier transform infrared studies of the clays were carried out to identify the functional group present on the clay. Figure 3 shows the IR spectra of the Na-MMT, Claytone HY and silane-MMT clay. In case of IR spectra of Na-MMT [Fig. 3(a)] a weak band at about 3630 cm^{-1} is due to lattice hydroxyls OH stretching mode, which arises from the vibration of firmly bounded H_2O . Also strong broad band at 3430 cm^{-1} can be attributed to the H—O—H stretching vibration of H_2O readily lost upon heating. This band reflects the free H_2O adsorbed onto the structure and/or interlamellar water OH stretch. The band near 1630 cm^{-1} is due to the water of crystallization bending vibration.

The strong band near 1115 cm^{-1} is due to Si—O bending vibration. The Si—O—Si stretching vibration

appears near 1045 cm^{-1} as a strong band. The 920 and 850 cm^{-1} band is due to Al—OH and Mg—Al—OH, respectively. The weak band near 800 cm^{-1} is attributed to the vibration of the quartz. The IR spectra of Clayton HY shows bands at 2924 and 2853 cm^{-1} (assigned to symmetric and asymmetric stretching of CH_2 , respectively) and at 1469 cm^{-1} (due to flexural vibrations of CH_3). These results indicate that the quaternary ammonium salt molecules are incorporated into the clay structure. The IR spectra of silane modified clay (silane-MMT) showed the peak at 1561 cm^{-1} indicates N—H bending, due to amino groups attached with silane. It is known that the silanol groups of aminopropyltrimethoxy silane coupling agent generated by hydrolysis of alkoxy groups react with hydroxyl groups on the silica particle surface via dehydration and condensation to form siloxane bonds. By such treatment, the functional groups of silica (—OH) are partly converted into amino terminal groups with extended organic chains on the silica surface.

Wide angle X-ray analysis of filaments

Figure 4 shows the XRD patterns of nylon 6 and nylon6/clay nanocomposite filaments after heat setting and drawing. The drawing and heat setting of the filaments was done at 65 and 115°C, respectively. It has been observed that filament samples (nylon 6 and nylon6/clay nanocomposite filaments) exhibited two α crystalline peaks at 20.2° and 23.2° . In case of nylon/clay nanocomposite filaments the γ crystal

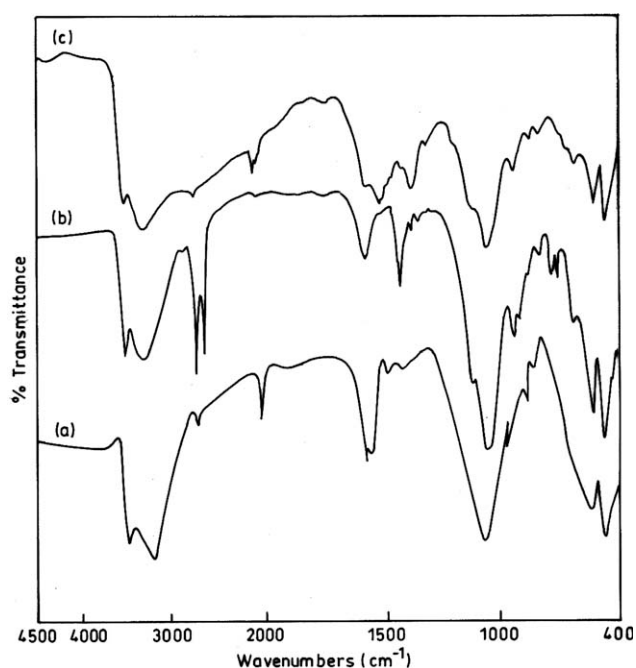


Figure 3 FTIR spectra of (a) Na-MMT clay, (b) clayton HY clay, (c) silane-MMT clay.

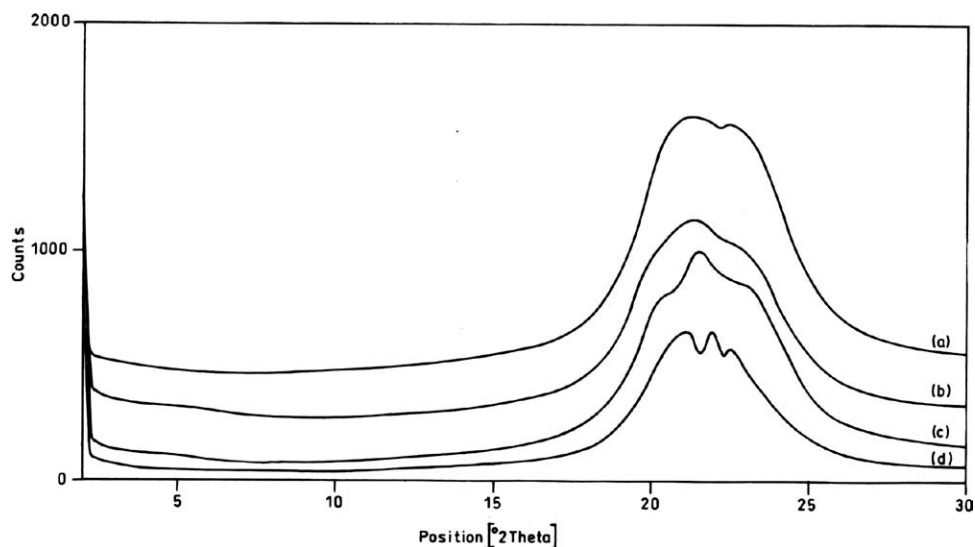


Figure 4 X ray diffractogram of (a) nylon, (b) nylon-Na-MMT, (c) nylon-silane MMT, (d) nylon-claytone HY filaments. The drawing and heat setting of the filament was carried out at 65 and 115°C, respectively.

form is dominant. It has been reported that the addition of clay promotes the formation of γ crystal form as the presence of the aluminosilicate layers stabilizes the pleated-sheet γ -crystal phase.¹⁷ As the silicate concentration increases, the volume of polymer at a sufficient distance from the silicate surface increases. Thus, retarding the process of chain folding, thereby, not allowing the formation of the α phase. Therefore, the γ phase forms near the silicate surface and the α phase forms at a distance removed from the silicate surface where the ability of the chains to fold remains undisrupted.

The percent crystallinity of the filaments is evaluated from the total area under the curve (A_t) and amorphous area (A_a) from XRD diffraction curves and the data is summarized in Table I. It is clear that the incorporation of the different kinds of clay increases the percent crystallinity of the nylon/clay nanocomposite filaments over the neat nylon filaments. With clay incorporation there is also a possibility of increase in the number of nucleation sites which results in to smaller crystals formed in large numbers as reported by other researchers working nylon clay nanocomposite fibers.¹⁵

Morphological structure of filaments

The morphological structure of the nylon and nylon clay nanocomposite filament were analyzed using scanning electron microscopy and shown in Figure 5. The neat nylon filament shows a striated structure [Fig. 5(a)] where the elongated units are seen arranged parallel to the fiber axis. It is known that, at high draw ratios, the folded chains of the crystallites are pulled out and forms a fibrillar network.²⁷ However in this study the striated morphology is

observed at moderate draw ratio of 5–6. The addition of the clay in nylon matrix changes the surface morphology of the filament as shown in Figure 5(b–d). The Na-MMT loaded nanocomposite filament show high agglomeration on the surface [Fig. 5(b)]. The Claytone HY filled nylon nanocomposite filament shows that the clay nanoparticles are mostly dispersed with in the nylon matrix [Fig. 5(c)]. However in some area they have got agglomerated. This may be due to the bundling of clay tactoids. It is also seen that while Clayton HY-based filaments shows a fibrillar structure similar to neat nylon but Na-MMT and silane-MMT-based filaments do not show such fibrillar morphology. This may be due to varied extent of drawing possible in different nanocomposite filaments depending on kind of interaction between the clay and the nylon matrix. The nylon nanocomposite prepared by silane MMT clay shows a well dispersed clay nanoparticles. To investigate the dispersion of silane-MMT clay in nylon matrix a very thin section of the cross section of the filament was cut and observed under TEM. The TEM picture (Fig. 6) shows that the layers of the silane-MMT clay get intercalated as well as exfoliated indicating a uniform dispersion.

TABLE I
Effect of Clay Addition on Percent Crystallinity of Nanocomposite Filaments

Type of filament	% Crystallinity ^a
Nylon	48.5
Nylon-NaMMT	57.3
Nylon-Clayton HY	57.6
Nylon-Silane MMT	58.3

^a Calculated from XRD data.

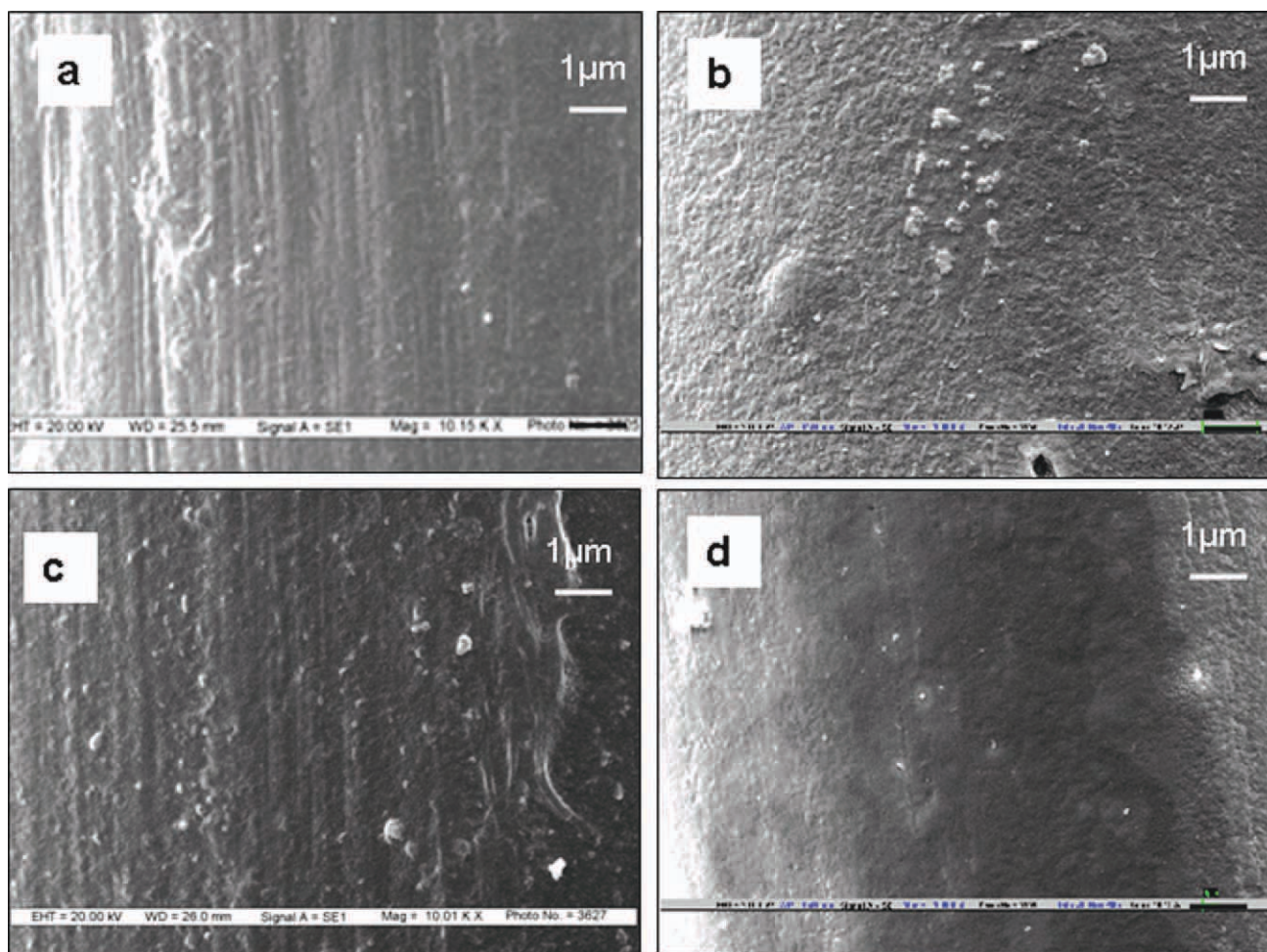


Figure 5 Scanning electron photographs of (a) Neat nylon (draw ratio: 6), (b) Na-MMT clay loaded (draw ratio: 5), (c) clayton HY loaded (draw ratio: 5.5), (d) Silane-MMT loaded (draw ratio: 5.5) nylon nanocomposite filaments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Tensile testing of filaments

The tensile strength was measured for the nylon and nylon clay nanocomposite filaments and the results

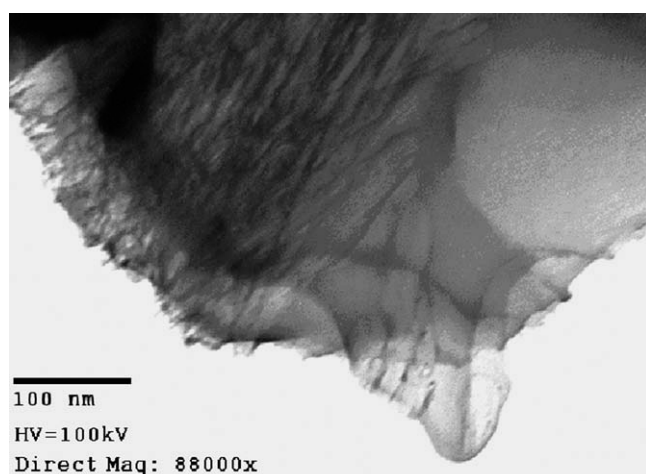


Figure 6 Transmission electron micrograph of cross section silane-MMT loaded nylon filament.

are summarized in Table II. The tensile strength of composite filament with Na-MMT decreases as compared to neat nylon filament. This may be due to highly hydrophilic nature of Na-MMT clay which is not compatible to the nylon matrix and this leads to agglomeration of clay platelets resulting in poor interaction and interphase. The tenacity of Claytone HY-filled nylon nanocomposite filaments showed also a marginal decrease in tenacity. The reason seems to be that imperfect bonding and debonding which occurs at interface due to incompatibility between the clay and polymer can not sustain the large interfacial shear stress that develops as a result of an applied strain, resulting in decrease in strength. Additionally, the drawability of the nanocomposite filaments is also adversely affected by clay agglomerates present in Na-MMT composites, decreasing the overall tenacity. In case of both the organo modified clay Claytone HY and Silane-MMT, however, the dispersion is more homogeneous as these are organomodified clays and have better compatibility with polymer matrix and therefore the

TABLE II
Tensile Testing of Nylon and Nylon/Clay Nanocomposite Filaments

Sample	Filament fineness (Tex)	Modulus (N/Tex)	Tenacity (N/Tex)	% Change in tenacity	Elongation (%)
Nylon	5.6	4.4	0.48	–	18.4
Nylon-NaMMT	6.5	4.4	0.37	Decrement (30%)	20.8
Nylon-clayton HY	5.7	4.5	0.45	Decrement (7%)	18.6
Nylon-silane MMT	5.3	4.5	0.53	Increment (10%)	18.3

Machine draw ratio = 5.5, CV% was within 4–5% for all samples listed here.

drawability is better than Na-MMT and reflects in higher tenacity values.

However, the silane MMT filled nylon clay nanocomposite filaments shows a 10% improvement in tenacity as compared to nylon filament. This may be due to better bonding between clay and nylon as the silane-treated clay provides additional sites (hydroxyl groups of silanol) for bonding with the nylon matrix, and thus help in sharing the load during tensile testing. Similar trends have been reported by other researchers with organic modified clays in case of nylon6/clay nanocomposite filaments.^{16,17}

Creep testing of filaments

Creep is a time-dependent plastic deformation, which takes place under stresses lower than the yielding stress of materials. Poor creep resistance and dimensional stability of thermoplastics is a barrier for their further expansion of applications, e.g., in the automotive industry. Recently it has been observed that the addition of nanoparticles in the polymer matrix improves the creep resistant property of the polymer.^{28,29} Hence, the creep behavior of nylon and nylon clay nanocomposite filaments has been studied and the data is summarized in Table III. It is clear that the creep tendency of nylon filament decreases significantly after the addition of different kinds of clay. The silane MMT incorporated nylon nanocomposite filament showed a 19% improvement in the creep resistance tendency as compared to neat nylon filament. The creep behavior of nylon filament is related to its viscous or amorphous portion. The addition of clay imparts rigidity to the polymer and therefore reduces the creep tendency of nylon nanocomposite filaments. The silane MMT

TABLE III
Creep Behavior of Nylon and Nylon Clay Nanocomposite Filaments

Sample	Creep (%)
Nylon	8.4
Nylon-NaMMT	7.6
Nylon-clayton HY	7.6
Nylon-silane MMT	6.8

At 10% breaking load and time 24 h, CV%: 0.1%.

clay also forms crosslinks with the nylon polymer chains and thus restricts the mobility of the chains in the amorphous region, resulting into a significant improvement in the creep resistance behavior of the nylon nanocomposite filament over neat nylon filaments. The nano clays restrict the slippage, reorientation, and motion of polymer chains, thus reducing the resultant creep strain. The improvement in percent crystallinity of the nylon clay nanocomposite filaments as compared to nylon filaments as revealed in WAXD study further results in improvement in these properties. Similar kinds of results have been observed by the Zhou et al.,²⁹ on incorporation of silane coupling agent treated SiO₂ nano particle in case of polypropylene nanocomposite.

Tensile properties of cords

The tensile strength of the cords prepared from nylon and different nylon clay nanocomposite filaments was measured and presented in the Table IV. It is observed that the cord prepared from nylon NaMMT nanocomposite filament showed a marginal decrease in tenacity as compared to nylon cord. The cord prepared from nylon Claytone HY and Nylon-silane MMT nanocomposite filaments showed a higher tenacity as compared to nylon filament cord. However the elongation percentage decreases marginally with the addition of clay.

H Adhesion test for cords

The interfacial adhesion strength between the cord and rubber matrix is an important parameter for the

TABLE IV
Tensile Results of Nylon and Nylon/Clay Nanocomposite Filaments Cords

Sample	Cord fineness (Tex)	Number of filaments	Tenacity (N/Tex)	Elongation (%)
Nylon	145.4	24	0.43	23
Nylon-NaMMT	146.2	24	0.41	22
Nylon-clayton HY	146.6	24	0.46	21
Nylon-silane MMT	147.4	24	0.53	18

CV% was within the range 4–5% for all the samples listed here.

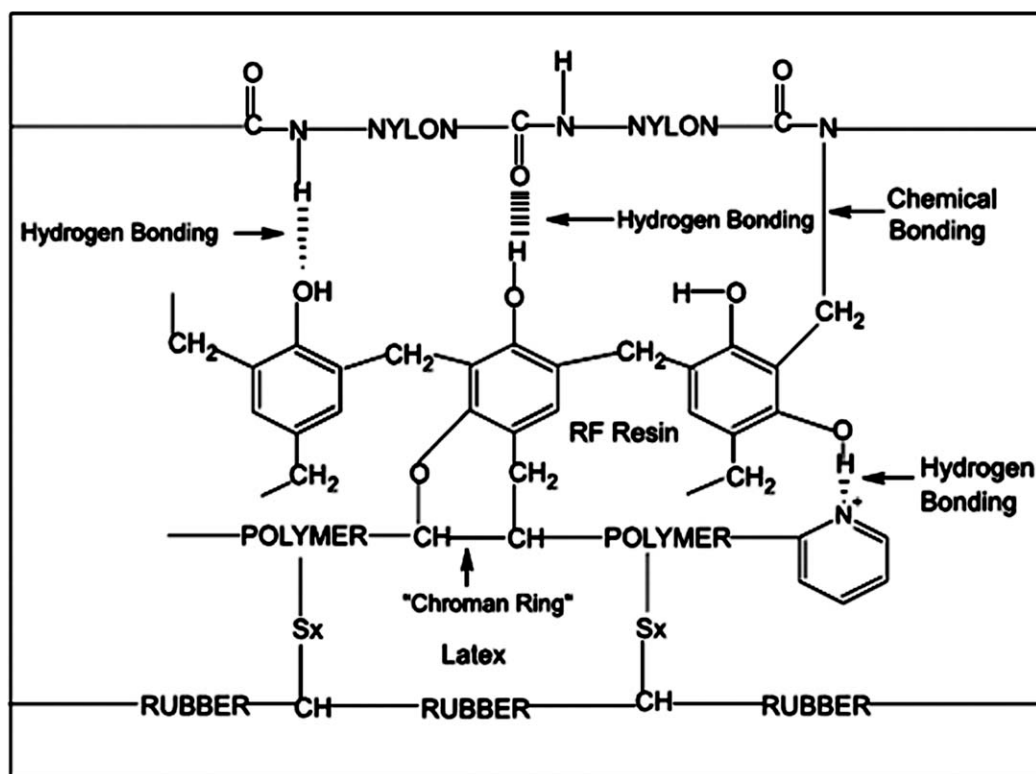


Figure 7 A possible mechanism for the bonding of RFL dipped nylon fibers to natural rubber.

performance characteristics of the tire cord. In the case of Nylon-6 tire cords, the polar cord shows poor adhesion to the nonpolar rubber matrix. To improve the adhesion between these two dissimilar surfaces, tire cords are dipped into resorcinol formaldehyde latex (RFL) so as to form a coating. RFL is a blend of resorcinol-formaldehyde resin and rubber latex (such as terpolymer of styrene, butadiene or natural rubber). The resin part adheres to the nylon cord whereas the latex part helps in bonding with the rubber matrix. A possible mechanism for the bonding of RFL dipped nylon fibers to natural rubber is shown in Figure 7. The mechanism of RFL-nylon cord adhesion is due to a combination of chemical bonding, hydrogen bonding, dipole-dipole interaction, and inter diffusion across the interface between RFL dipped cord and rubber.³⁰

The FTIR studies of Na-MMT and organomodified clays i.e., Silane-MMT and Clayton HY as discussed earlier showed already that additional hydroxyl (-OH) groups are present in Silane-MMT and quaternary ammonium group in Clayton HY. These functional groups give additional site for bonding between RFL to nylon cord.

The adhesion strength of nylon and various nylon clay nanocomposite cords with rubber using H adhesion test was measured and the data is presented in the Table V. It is observed that the addition of clay improves the adhesion property of nylon clay

nanocomposite cords with RFL and subsequently with the rubber. The addition of silane-MMT has improved the adhesion property by 34% over neat nylon cords. The silane coupling agent has hydroxyl group in its structure which helps in forming a covalent bond with RFL as shown in Figure 8(c), resulting in enhanced adhesion property.

The Clayton HY clay filled nylon nanocomposite filament cords showed a 55% improvement in the adhesion property as compared to neat nylon filament cords. Clayton HY contains quaternary ammonium compounds (as evidenced in FTIR) may provide additional sites for hydrogen bonding with RFL resulting in enhanced adhesion property as shown in Figure 8(b). The long carbon hydrophobic chain (tallow) attached to quaternary ammonium salt in Clayton HY may further enhance the Van-der-Waals bonding interaction with the latex part of RFL resin and the rubber.

TABLE V
H Adhesion Test for Cords

Sample	H adhesion force (N)	% Increment
Nylon	34	-
Nylon-NaMMT	36	5
Nylon-Silane MMT	46	34
Nylon-Clayton HY	53	55

An average of five specimens reported CV%: 4-5%.

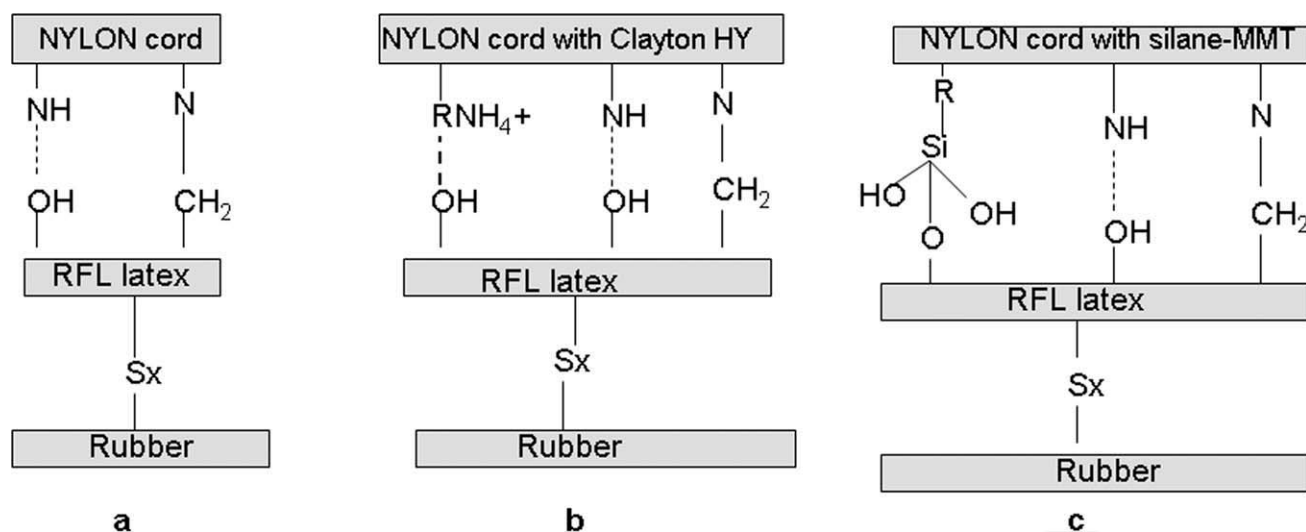


Figure 8 A schematic representation of possible bonds of RFL dipped (a) nylon filament cord, (b) nylon-clayton HY nanocomposite, (c) nylon-silane MMT nanocomposite filament cord with rubber.

Compression tension fatigue test

The results of the Goodrich block compression-tension fatigue test for the cords are summarized in Table VI. It has been observed that the addition of clay reduces the strength retention property of nanocomposite filament cord after 120-h compression test as compared to neat nylon filament cord. Cyclic loading in the rubber-cord test block leads to heat generation. This may be because at high temperature range nanocomposite filament cords have higher (than the nylon filament cord) dynamic mechanical loss due to more heat generation.

In this compression-tension fatigue test of the cords, the cords are not in a relaxed state but are in a stretched condition where the dynamic heat generation may affect the fiber molecular chains in different ways. The heat generated under dynamic stress causes thermochemical degradation and changes in the molecular structure. The fatigue resistance of cords is also generally controlled by several other factors such as twist, interfilament friction and cord

rubber adhesion.³¹ The inter filament friction may be higher in nylon 6/clay nanocomposite filaments as compared to neat nylon filament, leading to reduced fatigue resistance of nanocomposite cords. Moreover, the exposure of organomodified clay (Clayton HY as well as Silane-MMT) to high temperature or longer duration during this test may have led to thermal degradation of the organic part and thus lead to overall greater deterioration of strength as compared to nylon and Na-MMT nylon nanocomposite filaments.

CONCLUSIONS

This study demonstrates that nylon/clay nanocomposite filaments based on organo modified clays i.e., Claytone HY and silane-MMT show an improvement in tensile strength (10%) and creep resistant behavior (20%) as compared to the neat nylon and nylon/Na-MMT nanocomposite filaments. SEM and TEM results indicate a uniform dispersion and well intercalated structure in the nylon/clay nanocomposites based on clay organomodified clays i.e., Silane-MMT. The FTIR data of silane-MMT clay shows the presence of $N-H$ bending peak at 1561 cm^{-1} indicating successful penetration of aminopropyl trimethoxy silane groups in clay galleries and surfaces. The nylon/clay nanocomposite filament cords showed a 35–55% improvement in cord to rubber adhesion property as compared to neat nylon filament cord as revealed by H adhesion test data. This may be due to the additional sites provided by the organic modifiers to bond with RFL latex. However, the nanocomposite filament cords showed an inferior fatigue resistance as compared to neat nylon filament cord.

TABLE VI
Compression Tension Fatigue Test for Cords

Samples	Breaking force (N)		% Retention
	Zero h (0 cycle)	120 h (11.16 M cycles)	
Nylon	403	372	92.2
Nylon-NaMMT	399	365	91.4
Nylon-silane MMT	414	353	85.3
Nylon-clayton HY	409	333	87.2

CV%: 3–5%.

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