

**STUDIES ON POLYURETHANE / CLAY NANOCOMPOSITE  
FILAMENTS**

by

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**DEPARTMENT OF TEXTILE TECHNOLOGY**

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in fulfillment of the requirements of the degree of Doctor of Philosophy*

to the



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*Dedicated To My Parents*

## Certificate

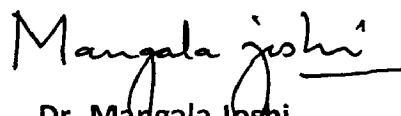
This is to certify that the thesis entitled “**Studies on Polyurethane / Clay Nanocomposite filaments**” being submitted by Mr. **G.V Raghunath Reddy**, to the Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy** in the Department of Textile Technology is a record of bonafide research work carried out by him. Mr. Raghunath Reddy has worked under our guidance and supervision and fulfilled the requirements for the submission of the thesis.

The results contained in the thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree or Diploma.



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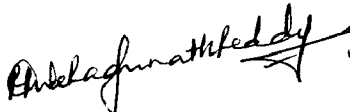
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## ABSTRACT

This thesis is an attempt to explore the feasibility of producing filaments from polyurethane (PU) /clay nanocomposites and compare their structure and properties vis-a-vis neat PU filaments. This work reports the production of filaments from neat polyurethane and polyurethane/clay nanocomposite by dry-jet-wet spinning; a technique being used for the first time for this system. Commercially available organomodified nanoclay is used as filler and thermoplastic polyurethane as the matrix.

Box-Behnken design has been used to optimize the spinning parameters of dry-jet-wet spinning of neat PU. Influence of dope solid content, dry-jet length and shore hardness of PU, on the mechanical properties of filaments are also addressed.

The effect of ultrasonication on size, size distribution and stability of clay dispersion as well as rheology and isothermal phase separation characteristics of PU/clay nanocomposites have been studied. The studies demonstrate the need for preparation of good dispersion of organomodified clay and effect of ageing on dispersion stability. This also emphasises the need to remove coarse clay particles to ensure optimum results. Rheological studies demonstrate the behaviour of polymer dope on incorporation of varying amounts of clay dispersion. It also speculates the possible state of nano material dispersion while in solution. Isothermal phase diagrams reveal the reason for the behavioural change of varying shore hardness of different grade of PUs and also the influence of temperature. Other important results relate to the impact of the state of nanoclay particles and its concentration on the phase separation characteristics of PU/clay nanocomposite.

The PU/clay nanocomposites are prepared by solution intercalation technique. The nanocomposite dope is spun into filament form by dry-jet-wet spinning. Nanoclay concentration varied in the range of 0.25 to 1.25 wt %.

The morphology of the nanocomposites was investigated using X-ray diffraction, Differential Scanning Calorimetry, SEM, TEM, AFM, and ATRFTIR characterization techniques. The PU/clay nanocomposite filaments have been evaluated for their density, sonic modulus, mechanical, thermal (DSC, TGA & TMA) properties, boiling water shrinkage, water swelling, fire retardant characteristics (in film form by cone calorimeter), dyeing and weatherability. The morphological studies of these nanocomposite filaments reveal a lot of interesting findings. XRD and TEM analysis show that at low clay loadings (0.25 wt %), clay platelets are highly exfoliated and finely dispersed in the PU matrix. At higher clay loading (1.0 wt %), clay exist predominantly as flocculates/ aggregates along with exfoliated and intercalated dispersion domains. Dispersed nanoclay in PU matrix has induced both external morphological changes as well as internal micromorphology. Nanoclay dispersion reduces the stretchability by enhancing the void content of the nanocomposite filaments. Modulus and tenacity are enhanced significantly in the presence of nanoclay at low concentrations; nevertheless elongation and elastic recovery are marginally affected. At low extension of 100-150 %, the low clay containing nanocomposite fibres demonstrated superior elastic recovery properties. Thermal studies suggest that a significant improvement in thermal stability of PU/clay nanocomposites filaments is due to hybridization with inorganic nanoclay. High thermal shrinkage at low clay concentration indicated high orientation due to good dispersion and exfoliation of clay in filaments. Boiling water shrinkage and water swelling also indicated high orientation and reduced swelling due to incorporation of clay. Fire retardant properties studied by cone calorimetry shows excellent fire retardant

properties at low clay content (0.25 wt %). Dyeability properties of nanocomposite fibres also get significantly enhanced in the presence of nanoclay. Weatherability resistance of PU/clay filaments are significant only at higher clay concentration (~ 1 wt %).

This study thus reveals that by incorporation of small amounts of inorganic nanofillers i.e. nanoclays in the PU matrix, a significant improvement in properties such as initial modulus, tenacity, thermal stability, fire retardant and dyeability can be achieved in nanocomposite filaments. However, dispersing the clay at nanolevel is the key for potential property realization in the final nanocomposite. This study also reveals that dry-jet-wet spinning can be useful alternative technique for spinning of neat PU as well as PU/ clay nanocomposite filaments.

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