National Textile Center

FY 2003 (Year 12) Continuing Project Proposal

Project No. M02-MD08

Competency: Materials

Nano Engineered Fire Resistant Composite Fibers

Project Team:

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Objective:

The objective of the research is to obtain a molecular level understanding of thermal stability and degradation of heat and fire resistant polymeric composite fibers embedded with nano-scale hard particles. Heat transmittance through nylon rich composites under exposed flame or high temperature is complex due to the various modes of heat transfer. These research addresses issues related to the mechanisms of heat/flame propagation through polymer-filler assemblies via overall structural investigation and interfacial interaction between nanoparticle and polymer phases. Hence, link between microstructural parameters and thermo-mechanical behaviors will be established by developing heat penetration model that takes into account various modes of heat supply and their influence on final fiber geometry.

Relevance to NTC Mission:

The competitiveness of US fiber industry has been declining for at least the last decade. Lack of fundamental understanding of structure/property/process relationships has affected the industry where research has largely been focussed on either process or product development. Existing industrial fiber research emphasizes comprehensive characterization of the final product, but often lacks in scientific correlation between the process and the product. Since the properties of the fiber depends on the history of structure development, scientific studies to elucidate structure/process relationships is necessary to lead to breakthrough technologies. This project is in concurrence with all three NTC goals since it involves "…innovative and improved manufacturing process…", "...trained personnel, industrial partnerships, and transfer mechanisms" and "…strengthen the nation's textile research and educational efforts". Proposed research is directed at understanding the processing of flame resistant nanocomposite fibers and to visualize the molecular structure and superstructures responsible for flame retardation process. We believe that this study will be vital to enhance the technical competitiveness of the U.S fiber industry and eventually lead to rapid development of new products.

Progress Statement:

We undertook the investigation of fire resistant nanocomposite fibers by: (1) in situ polymerization of monomer/ nanoparticle mixture through the formation of in situ intercalated inorganic-organic hybrid composite, (2) melt mixing and melt intercalation of nanoparticle and fiber forming polymers in Brabender single screw extruder and (3) processing of RTP company nylon 6 based nanocomposite granules through fiber formation and their characterization in terms of thermal stability. We obtained in situ intercalated inorganic-organic hybrid from ε-caprolactam polymerization of nylon 6 within the intercalated laponite nanoparticles. We extruded nylon 6/zeolite composite fibers by inserting zeolites and structurally compatible nanofillers into polymer melt. The extrusion was carried out at 230°C using a screw speed of 20 rpm and 1/32 inch die diameter and the extruded polymer melt was drawn by the winder and winded through the bobbin at the rate of 200m/min. Commercially available nylon 6-based nanocomposite granular masterbatch was also extruded as composite fiber by Brabender extruder. Most of the recent in-situ intercalative polymerization techniques require the modification of the layered silicates in order to improve the polymer layered silicate compatibility. We polymerized nylon 6 in the presence of 4.8% laponite clay in spite of its strong hydrophilic nature. During in-situ polymerization experiments we observed that the oxygen in

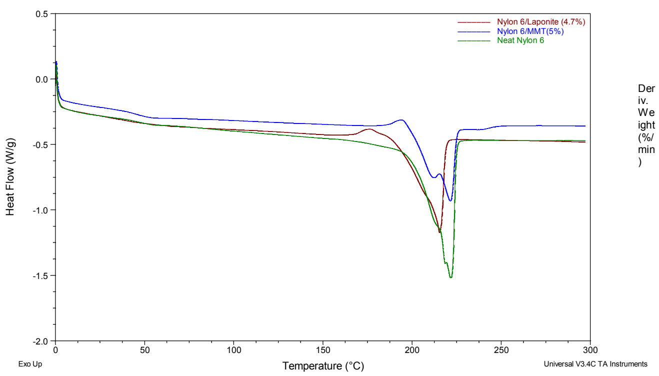

Figure 1 DSC curves of neat nylon 6, nylon 6/laponite, and nylon 6/montmorillonite composites under 10^0C/min heat flux

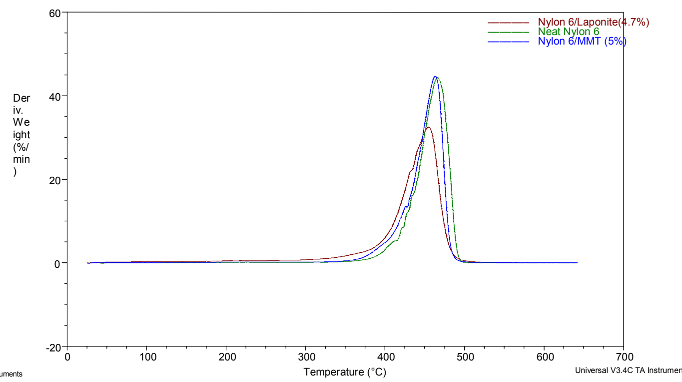

Figure 2 Mass loss rates of neat nylon 6, nylon 6/montmorillonite (5%), and nylon 6/laponite (4.7%) composites

the air has strong influence on the polymerization process. Experiments done in air atmosphere resulted in severe degradation of the resulting product. Amount of bound water on the laponite surface and free water between the laponite-monomer interphase seemed to influence the ring opening mechanism of ε-caprolactam. Precise temperature control is required to achieve controlled polymerization. Thermal properties of neat nylon 6, nylon 6/laponite clay and nylon 6/montmorillonite nanocomposites were determined by TA instruments Differential Scanning Calorimeter DSC Q 1000 and Thermogravimetric Analyzer, TGA Q500. As shown in figure 1, DSC measurements indicate that the presence of a smectite filler, whether laponite or montmorillonite, result in similar but slightly decreased melting points compared with neat nylon 6. TGA results shown in figure 2, indicate that in situ polymerized nylon 6/laponite nanocomposite sample has lowest decomposition (mass loss) rate and the highest carbonaceous residue (reference annual report) compared to the neat nylon 6 and nylon 6/montmorillonite nanocomposite. Although we could not achieve expected disintegration and dispersion of zeolite agglomerates in melt extrusion of nylon 6/zeolite nanocomposite fiber but we observed improved char formation in the composite compared to the neat polymer. The char formation and reduced decomposition rate may have an effect conducive to improved fire resistance behavior of the materials [1].

Approach:

Nanocomposite technology is an entirely new generic approach to reduce or resist the flammability of polymeric materials using environmentally friendly nano size additives. In the proposed work we aim to investigate and model at a molecular level the heat and flame transmittance into fibers containing nano particles and thereby design new nano engineered composite fibers with improved properties. In a clay- polymer (nylon) nanocomposite the clay particles are about the same size as the polymer molecules themselves so they are likely to be intimately mixed and chemically bonded to each other [2]. This has the overall effect of increasing the thermal stability and viscosity of the polymer while reducing the transmission of fuel gases during burning. The result is a 60-80% decrease in rate of heat released from a burning polymer nanocomposite containing 2-6% of clay by weight. Flame-retardants added to a polymer may tend to degrade mechanical properties however in polymer- clay system it has been observed that the addition of 2-6% of clay in nylon does not affect the mechanical properties of composite fiber; rather, it doubles the mechanical strength. Thus extraordinarily high degree of fire retardant efficiency of nylon nanocomposite fibers stems from the intimate interaction between nano clay (or nano size other flame retardant additives that reduce the smoke and toxic gas emission. These polymer nanocomposites have twice the stiffness and strength of the original material and a higher softening temperature [2,3]. Nylon, owing to its low thermal conductivity, is a potential polymer to prepare flame resistant polymer-ceramic particle nanocomposite. Nylon-montmorillonite composite provides flame resistance by producing a unique kind of char. When the polymer burns, the residue consists of alternating layers of silicate and carbon char, a combination that might have an unusually good insulating property.

Inorganic fire retardant based on zirconia and boron oxides are highly efficient, environmentally benign additives which reduce heat release rate to a great extent in commodity (nylon, polyethylene, polypropylene) and engineering (cyanate esters, ULTEM, PEI) polymers at a low concentrations without increasing smoke and carbon monoxide. The second phase of our research will be to explore suitable combinations of additives to ensure a synergistic effect for improved heat and flame resistance. We shall establish mechanisms of the heat and flame retardation processes. Surface active flame-retardants concentrate at a burning polymer surface, interfacial free energy being the driving force. Migration of surface active flame retardants from the bulk to the burning surface improves flame retardant efficiency by reducing loading level required for the fire resistance.

Several experiments based on thermophysical properties relevant to thermal stability will be conducted over a range of temperature. These will include thermal conductivity, gas permeability, thermal expansivity, limiting oxygen index, smoke density and toxicity of the nano engineered composite fiber. Microstructural characterization will include the study of interfacial bond strength, particle connectivity, pore size and pore shape. Techniques used to study these parameters will include image analysis and nanoindentation. FTIR will be used to detect gases produced by burning composite fibers. Thermogravimetric analysis and differential scanning calorimetry will be used to investigate thermal stability and degradation study of fibers. Certain mechanical properties will be measured at room temperature. Attention will be on tensile and compressive strength, Young's modulus and Poisson's ratio

The final stage of our program will be the development of a 3-D heat penetration model, which will quantify the heat transfer in the fiber. In our modeling effort thermal conduction, gas permeation, material volatilization, chemical changes and structural geometry of the fiber will be taken into account [4]

Reference

1. P. K. Patra, S. B. Warner, Y. K. Kim, Q. Fan, S. Adanur, G. Inan and B. Ascioglu , annual report no M02-MD08 submitted to NTC Oct 2002
2. E. P. Giannelis, Flame retardant nanocomposite materials, NIST Annual Conference on Fire Research, Gaithersburg, MD (1998)
3. FAA Fire Research, "Targeted areas of Research " (1999)
4. C. F. Cheng, Y. C. Tsui and T. W. Clyne, Application of 3-D heat flow model to treat Laser Drilling of Carbon fiber Composites, *Acta Metall. et Matter.,* 46 (1998) 4273-4285

This Year's Goal:

We are investigating the effects of layered silicates of different structures and sizes on thermal and mass transport of nylon 6 polymer at different levels of decomposition. We will correlate the thermal and mass transport ability of char layer with virgin and semi-decomposed polymer to understand the structural changes during polymer pyrolysis and char formation for nylon 6 based nanocomposite. We have started Investigations on other polymer nanofillers systems (PP and PET). This year and in subsequent years we will perform molecular dynamics simulations of the thermal degradation of polymer nanocomposites in an attempt to explain the reduction in the flammability of nano-confined polymers as compared to the pure polymer

Outreach to Industry:

We are interacting with companies in New England area through our Advance Technology and Manufacturing Center (ATMC). We have presented our research in the annual sigma XI conference held at UMD in May 2002 and sent our findings to MRS spring meeting to be held in Sanfrancisco in April 2003. We have communicated to NTC our annual report that is available for diffusion to textile firms of U.S. Our team is in contact with many textile and polymer industries working on polymer-clay systems. The results from our development of structure/property relations will be of special interest to fiber manufacturers. This proposal addresses the growing concern in the US and abroad regarding fire resistant protective fabric products and their overall effect on human performance.

New Resources Required:

No new resources required.