

U.S. DEPARTMENT OF COMMERCE PROJECT:
NANOPARTICLE REINFORCED HYBRID FIBERS AND FILMS

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The objective of this research is to combine traditional polymeric materials with nanoparticles (e.g. carbon nanotubes and nanoclays) to engineer new hybrid polymeric parts and micro/nano fiber/film properties for nontraditional industries such as fuel cells and electronics using injection molding, extrusion and electrospinning processes.

Research Area 1: EFFECT OF PROCESSING PARAMETERS AND NANOCCLAY REINFORCEMENT ON POLYPROPYLENE FILM PROPERTIES

The new twin screw extruder was tried. Some polymers and nanoclays were stuck inside the twin screw extruder. The parts of the twin screw extruder were taken out and cleaned. Then some trial productions were done by using compatibilizer, polypropylene (PP) and nanoclay. However, since there was a problem with the thermocouples of the twin screw, good quality production could not be achieved. Besides, there was not any nanoclay feeder for the machine. Therefore, the production with nanoclay was challenging.

Nanoclay added films that are scheduled to be manufactured are listed in Table 1. Their mechanical and physical properties will be tested.

Table 1 Nanoclay added films and their contents

	Compatibilizer (%)	Nanoclay (%)	Compatibilizer (g)	Nanoclay (g)	PP (g)	Mixture (g)
Film 1	10%	1%	100	10	890	1000
Film 2	10%	3%	100	30	870	1000
Film 3	10%	5%	100	50	850	1000
Film 4	15%	1%	150	10	840	1000
Film 5	15%	3%	150	30	820	1000
Film 6	15%	5%	150	50	800	1000
Film 7	20%	1%	200	10	790	1000
Film 8	20%	3%	200	30	770	1000
Film 9	20%	5%	200	50	750	1000

Research Area 2: DEVELOPMENT OF COMPOSITE AND SANDWICH STRUCTURED FUEL CELL MEMBRANES

Experimental

Polymer electrolyte membrane fuel cell (PEMFC) membranes will be produced for high temperature applications. These membranes will be composite membranes or sandwich structured composite membranes.

To produce PBI composite and sandwich structured composite membranes, PBI polymer was synthesized. 3,3',4,4'-tetraaminobiphenyl, isophthalic acid, polyphosphoric acid, triphenyl phosphite, calcium chloride and potassium hydroxide were purchased from Sigma Aldrich. Calcium chloride drying tube was purchased from Fischer Scientific.

To synthesize PBI polymer, 3,3',4,4'-tetraaminobiphenyl and isophthalic acid was mixed in polyphosphoric acid and triphenyl phosphite. The reaction system consisted of a 250 ml four neck flask equipped with a calcium chloride drying tube and nitrogen inlet. Then the polymer obtained was neutralized with potassium hydroxide. More trials will be done in order to obtain more qualified PBI polymer.

Modeling

For high temperature polymer electrolyte fuel cell membrane having a PBI based membrane, a two dimensional mathematical model was developed. The model has three domains: anode, PEM and cathode. The governing equations of the domains were obtained.

Computational

COMSOL Multiphysics Software Package will be used for solving the equations of the two dimensional mathematical model of the high temperature polymer electrolyte fuel cell membrane having a PBI based membrane. These governing equations are coupled equations to be solved simultaneously and contain lots of nonlinearities that are hard to be solved analytically. Therefore, to learn how to use COMSOL Multiphysics Software Package, some trial solutions were done by using the software.

Research Area 3: REINFORCED FIBER EXTRUSION

New twin screw extruder was installed and used to produce nanoclay-polypropylene nanocomposite structures. It is known that twin screw extruders provide better mixing and shearing compared to single screw extruder. Nanoclay plates can be separated more efficiently with high shearing effect by using twin screw extruder.

Materials used during the experiments:

- Cloisite 15A
- 30 melt copolymer polypropylene with 34 g/10 min flow rate, and 0.91 g/cm³ density.
- Polybond 3200 (PP grafted with maleic anhydride; 1.0 weight % maleic anhydride level).

The parameters for the experiments are as follows:

Die zone 1	Die zone 2	Die zone 3	Die zone 4	Die zone 5	Die zone 6	Die zone 7
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200 ° C	200 ° C	200 ° C	200 ° C	220 ° C	220 ° C	220 ° C
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Motor speed	Feeder Speed
350 RPM	250 RPM

A feeder was used to feed polypropylene pellets into twin screw extruder hopper. Nanoclay particles and polybond 3200 were mixed before the experiments. 1% nanoclay and 10% Polybond 3200 were used in the system. This mixture was fed manually when polypropylene pellets were transferred to hopper.

Extruded polymer was cut with a small lab chopper to have pellets which contains nanoclay-polypropylene and polybond 3200. These pellets were extruded again in the twin screw extruder to obtain better dispersion and distribution of nanoclays in the polymer matrix.

The extruded pellets were analyzed with TGA and DSC to compare with pure polypropylene pellets. Figure 1 shows the decomposition temperatures of pure and nanoclay added pellets. The results indicate that decomposition temperature increased by addition of nanoclay particles. Nanoclays are known as good heat insulators and this caused higher decomposition temperature compared to pure PP pellets. Figure 2 shows the melting point of pure and nanoclay added pellets. It was observed that melting point decreased by almost 2 ° C with addition of nanoclays. This reduction was also observed with single screw extruder experiments. However, this time, reduction was more than the previous experiments. Better dispersion and distribution of nanoclays with twin screw extruder may have caused this difference. These pellets will be extruded with the single screw extruder to make monofilament yarns. Properties of these monofilaments will be compared with the previous experiments.

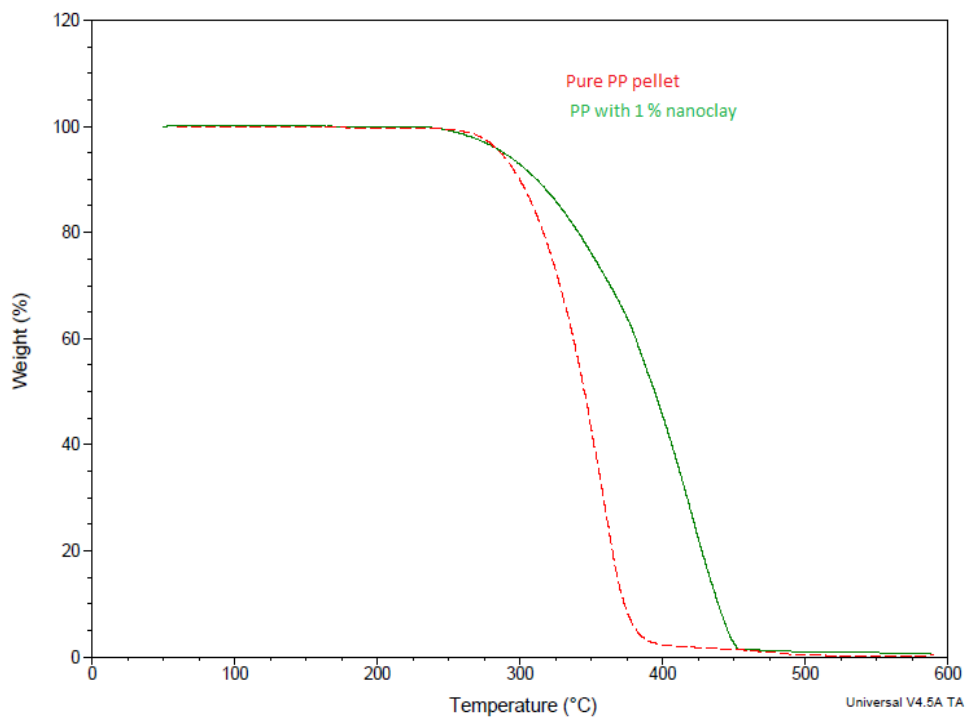


Figure1. Decomposition temperature of pure and nanoclay added pellets

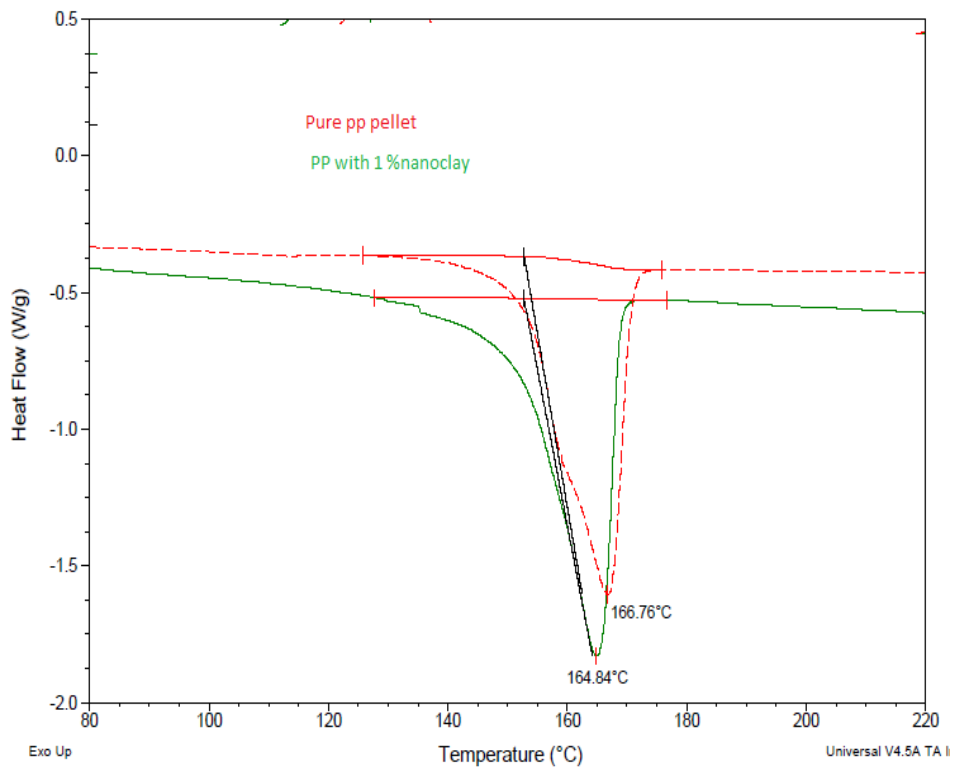


Figure 2. Melting temperature of pure and nanoclay added pellets

Research Area 4: TOUGHENING OF POLYPROPYLENE WITH THERMOPLASTIC ELASTOMER MATERIALS

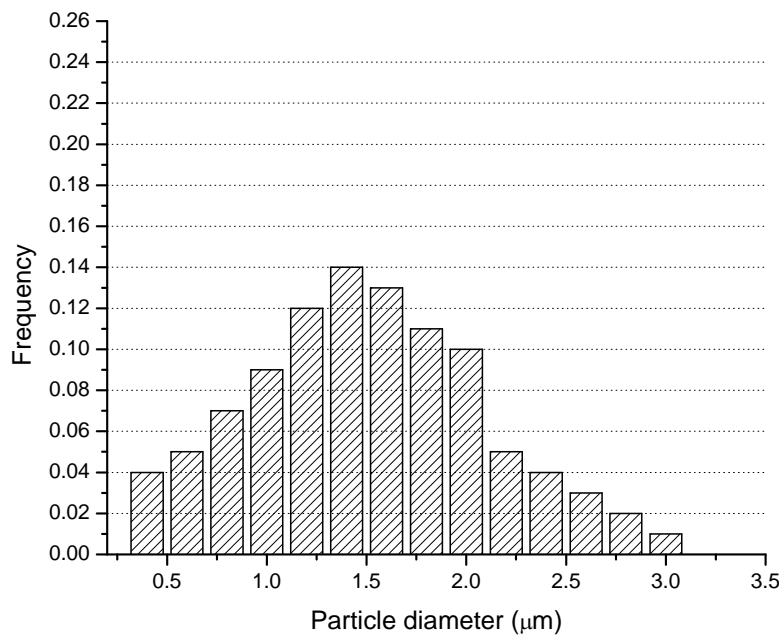


Figure 3. Histogram of F1 particle diameters in etched PP/F1 blend.

An article entitled “**Improving Toughness of Polypropylene with Thermoplastic Elastomers in Injection Molding**” was submitted to the Journal of Industrial Textiles and approved with some corrections to be done. The corrections are completed. The particle size distributions of F1 particles and F2 particles in etched samples are given in Figure 3 and Figure 4, respectively.

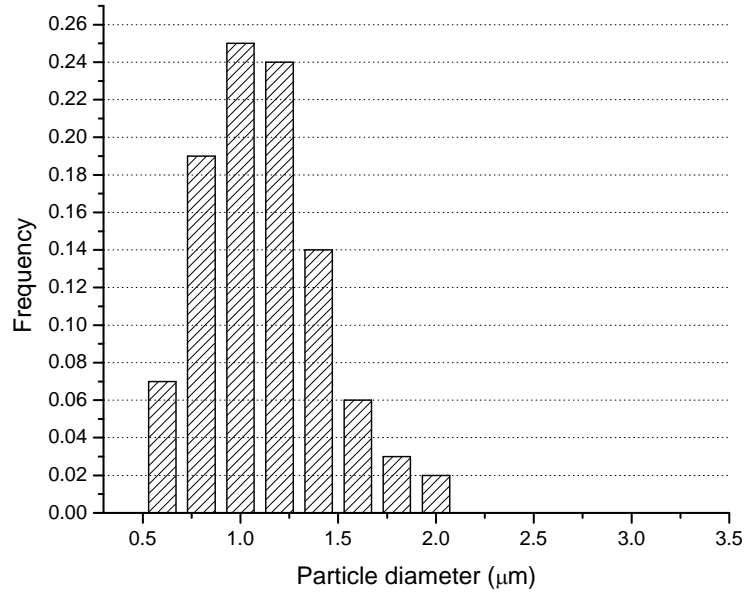


Figure 4. Histogram of F2 particle diameters in etched PP/F2 blend.

Sample volumes

The height and width of injection molded standard parts for tensile, impact and flexural strength tests were measured with a micrometer at six places for each sample. The average values were used to calculate the total volume of the samples. The surface of dog-bone shaped tensile strength samples was calculated considering the thick and thin places. Finally the total volume of dog-bone shaped samples was calculated.

Void content

Void content in a composite is one of the parameters that affects its properties. To investigate the effect of void volume on injection molded polypropylene parts reinforced with glass fibers and carbon fibers, the samples were weighed first. The samples were then dissolved in xylene in a hood and then filtered using graded papers. After filtering, fibers were washed with boiling xylene and left to dry. The effect of void volume on the resulting properties of the reinforced polypropylene samples will be investigated.

Research Area 5: SPI MEMBRANE FOR PEMFC APPLICATIONS

Abbreviations

SPI Sulfonated polyimide

PEMFC	Proton Exchange Membrane Fuel Cell / Polymer Electrolyte Membrane Fuel Cell
MEA	Membrane Electrode Assembly
FT-IR	Fourier Transform Infrared Spectroscopy
IS	Impedance Spectroscopy / Dielectric Spectroscopy
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscope

Overview

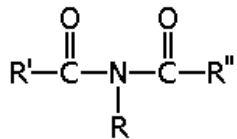
The 21st century is a time full of opportunity and challenge. With the highly developed economies and industries, global warming, greenhouse effects and environmental pollution have become the topic of discussion. The changes in the environment are, in varying degrees, the result of our own human activities. It is our established industry, traffic and housekeeping systems that bring pollution to our environment. Therefore, new power resources, new materials and greener industry are needed in the 21st century. Proton-exchange membrane fuel cells are believed to be one promising power source for their environmental friendliness in the 21st century for both stationary and mobile use.

New requirements of the materials in the proton exchange membrane

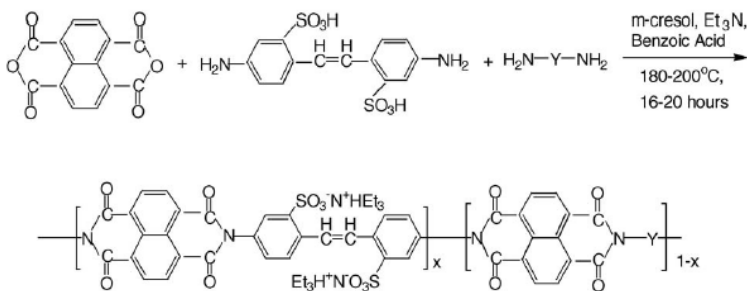
In recent years, the developments in design and manufacturing of fuel cell engines require new materials. The most popular proton-conducting membrane, DuPont's patented Nafion® which is a kind of sulfonated tetrafluoroethylene based fluoropolymer-copolymer, has some disadvantages such as high cost, low performance in low relative humidity and high temperatures.

Research objectives and methods

The goal of this research is to synthesize a new membrane which can work at higher temperatures and low humidity and have higher performance/price ratio than Nafion®. The target material is the SPI copolymers. Polyimides are high temperature engineering materials characterized by cyclic structures that contain imide groups in the polymer chains.

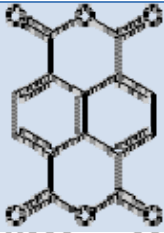
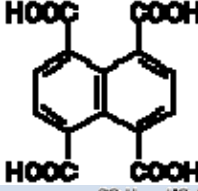
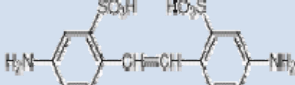
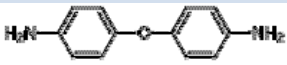
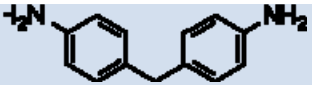
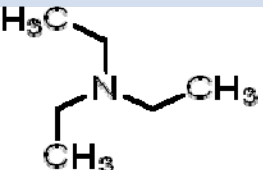

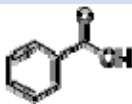


The first polyimide was produced in the early 1960s but only in recent years there has been a rapid development for high strength composites and thermally stable films. After sulfonation, it is believed to be a good candidate with high performance applications.



Synthesis of SPI copolymer

Raw material list

Chemical Name	Chemical Structure
1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA)	
1,4,5,8-Naphthalenetetracarboxylic Acid	
4,4'-Diaminostilbene-2,2'-disulfonic Acid (DSDSA)	
4,4'-Diaminodiphenyl Ether (ODA)	
4,4'-Diaminodiphenylmethane (MDA)	
Triethylamine	
3-Methylphenol (m-Cresol)	
benzoic acid	

Experimental process

NTDA, DSDSA, MDA and ODA were dried in a vacuum oven at 120°C overnight.

Synthesis of DSDSA-based SPI Copolymers

- DSDSA about 2.5g (7.0mmol) + m-Cresol about 50ml + triethylamine about 1.7g were added into 250ml dried 4-neck flask with stirring.
- The mixture was heated at 80° C under N₂ until DSDSA was completely dissolved.
- ODA about 0.6g (3.0mmol) + NTDA about 2.6g (10.0 mmol) + benzoic acid were added successively.

- 15ml m-Cresol was added.
- The mixture was stirred at 80°C for 4 hours, at 180°C for 16 hours and at 200°C for 4 hours.
- After cooling to the room temperature, 50 ml m-Cresol was added.
- The solution was precipitated into excess isopropyl alcohol (IPA) to filter and wash.
- Fiber-like copolymer was collected in the vacuum oven overnight.

Membrane preparation

- The copolymer was dissolved in m-Cresol.
- Membrane was formed by casting the solution onto a clean glass plate and dried at 120°C for 12 hours.
- By using shape razor blade, the membrane was collected after cooling down to the room temperature.
- The film was soaked in methanol at 60°C for 1 hour.
- The film was immersed in 1.5mol/L HCL at room temperature for 48 hours.
- The membrane was totally washed by deionized water and dried in a vacuum oven at 120°C overnight.

The SPI membrane has been made successfully, which has good mechanical properties, but there are still some problems with it, like the smoothness and uneven surface. Its properties need to be improved further.

Testing

After obtaining a satisfactory membrane, the following tests will be done: FT-IR spectra for characterization of element and bonding, impedance spectroscopy (IS) to measure the proton conductivity, thermogravimetric analysis (TGA) to measure the thermal stability, and scanning electron microscope (SEM) to get the surface picture of the membrane.

Journal Articles Submitted:

1. Keskin, R., and Adanur, S., "Improving Toughness of Polypropylene with Thermoplastic Elastomers in Injection Molding", submitted to Journal of Industrial Textiles, 1 December 2009, 26 pages.
2. Selver, E., and Adanur, S., "Processing and Property Relationship of Nanoclay Reinforced Polypropylene Monofilaments", submitted to the Journal of Industrial Textiles", 12 Nov. 2009, 19 pages.
3. Gocek, I., and Adanur, S., "Effect of Processing Parameters on Polypropylene Film Properties", submitted to Textile Research Journal, 3 Nov. 2009, 28 pages.

Conference Presentations Made:

4. Keskin, R., and Adanur, S., "Improving Toughness of Polypropylene Injection Molded Parts with Thermoplastic Elastomer Materials", The Fiber Society 2009 Fall Meeting and Technical Conference, The University of Georgia, Athens, GA, Oct. 28-30, 2009.
5. Gocek, I., and Adanur, S., "Effect of Processing Parameters on Polypropylene Film Properties", The Fiber Society 2009 Fall Meeting and Technical Conference, The University of Georgia, Athens, GA, Oct. 28-30, 2009.
6. Selver, E., and Adanur, S., "Processing and Property Relationship of Nanoclay Reinforced Polypropylene Monofilaments", The Fiber Society 2009 Fall Meeting and Technical Conference, The University of Georgia, Athens, GA, Oct. 28-30, 2009.