National Textile Center

FY 2003 (Year 12) Continuing Project Proposal

Project No.

C01-MD20

Competency: Chemistry

Dyeable Polypropylene via Nanotechnology

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Objective:

The main objective of this research is to study the feasibility of forming polypropylene fibers infused with nano particles that create dyesites to facilitate the dyeing of polypropylene materials. This modified polypropylene will actually be a nanocomposite polypropylene. Specific objectives are:

1. To select and/or develop nano particles that are able to form dyesites in polypropylene and have stability to high temperature (e.g. 200°C), and under normal dyeing and performing conditions.
2. To develop the dyeing and finishing processes for the nanocomposite polypropylene.
3. To evaluate and modify the properties of the dyed/finished materials.
4. To investigate the fundamentals in the formation of textile fiber from the nanocomposite polypropylene.
5. To examine and improve the physical properties of the resultant fibers

Progress Statement:

It was demonstrated in our last Annual Report that nanoclay does create attractive dye sites in the PP nanocomposite. It was also stated that dyeings of the resultant PP nanocomposites were uneven indicating that nanoclay is not properly dispersed in PP matrix. The factors behind the drawbacks were broad distribution of particle size and poor dispersion of nanoparticles in the polypropylene matrix.

A combined process of ball milling and sonication was carried out to reduce the particle size and to narrow the size distribution. In the ball milling operation, the speed of the tumbler was maintained at 20 rpm. The slow speed is preferred in order to increase the possibility of the balls making contact with many particles; hence the impact energy is even and the centrifugal forces would not overcome gravity. The weight ratio of balls to clay particles in the tumbler media was 40:1. The milling was carried out for 24 hours. The Particle Size Distribution (PSD), Specific Surface Area (SSA), Surface Weighted Mean Size (SWM), and Volume Weighted Mean Size (VWM) of As-received particles and ball-milled particles were then determined using a Particle Size Analyzer. Among these properties, SWM is very sensitive to the presence of fine particles, and VWM shows the sensitivity to the presence of coarser particles.

	As-received nanoclay particles	*3mm-Glass balls milled nanoclay particles*	*5mm-Glass balls milled nanoclay particles*	*4.76mm-Stainless steel balls milled nanoclay particles*	*8mm-Stainless steel balls milled nanoclay particles*
PSD	0.02 to 2000 μm	0.63 to 14 μm	0.35 to 41 μm	0.44 to 50 μm	0.44 to 55μm
SSA	1.22 m^2/g	2.92 m^2/g	2.55 m^2/g	2.20 m^2/g	2.35 m^2/g
SWM	4.900 μm	2.052 μm	2.348 μm	2.724 μm	2.548 μm
VWM	8.451 μm	3.172 μm	4.818 μm	5.830 μm	5.762 μm

Table I Effect of Ball Milling on the Size of Nanoclay Particles

The particles size distribution curve is shown in Figure 1. From Table I and Figure 1 it is evident that 3mm glass balls give better results than the other balls used.

In the sonification operation, 90% amplitude, 5 second on and 5 second off pulsation rate, and 4 hours time were found to facilitate effective reduction of particle size and size distribution. The sonicated nanoclay particles (after both ball milling and sonification) were obtained in nanometer dimensions as shown in Table II and Figure 2.

	As-received nanoclay particles	(Milled + Sonicated) nanoclay particles
PSD	0.02 μm to 2000 μm	50 nm to 350 nm
SSA	1.22 m^2/g	48.2m^2/g
SWM	4.900 μm	128 nm
VWM	8.451 μm	650 nm

Table II Effect of Sonification on the Size of Nanoclay Particles

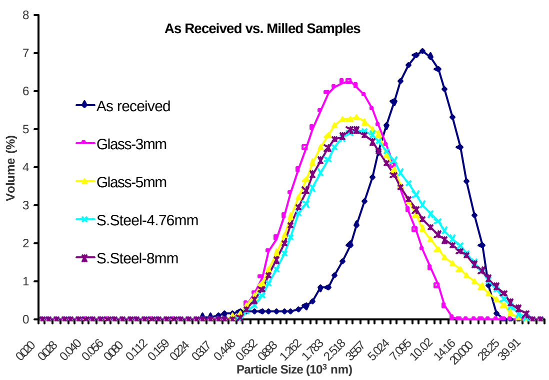

Figure 1 Particle Size Distributions of the As-received and Milled Nanoclay particles

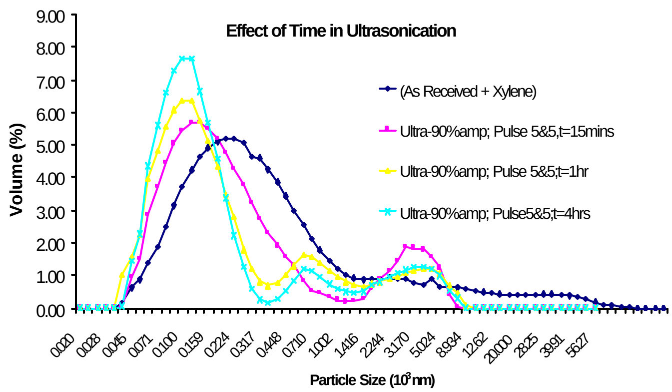

Figure 2 Particle Size Distributions of the As-received and Milled+Sonicated Nanoclay particles

It was found that the titanate coupling agent could help to establish a good linkage between polypropylene and the inorganic nanoclay particles. Titanium IV neoalkoxy tris(diisooctyl) phosphato-O (see Fig. 3) was used in the preparation of the PP nanocomposite. RO- group is compatible with the nanoparticles and -C_8H_{17} thermoplastic group is compatible with polypropylene. There is also a great possibility for the exfoliation of nanoclay particles because of the bulkier chemical structure group and its compatibility with the surfactants used in the modification of nanoclay particles.

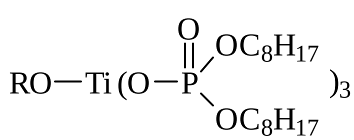

Figure 3 Structure of Titanate Coupling Agent

In order to determine the effect of titanate coupling agent, an experiment was carried out by using nanoclay particles as a filler in mineral oil. 0.375 % (w/v) of coupling agent reduced the viscosity of the mineral oil system from 3624 cps to 1430 cps as measured by a digital Brookfield viscometer.

Surprisingly, it was found that the dyeings of the newly prepared PP nanocomposites were very even in all the different types of nanocomposites and also the color yield increased considerably compared with the previous results shown in the last year annual report. It is concluded that the milling and sonification of the nanoclay particles in addition to the unique preparation with 0.4% (w/w) addition of titanate coupling agent contribute to the even dyeing of the PP nanocomposites. Some of the dyed PP nanocomposites samples are shown in Figures 4 and 5.

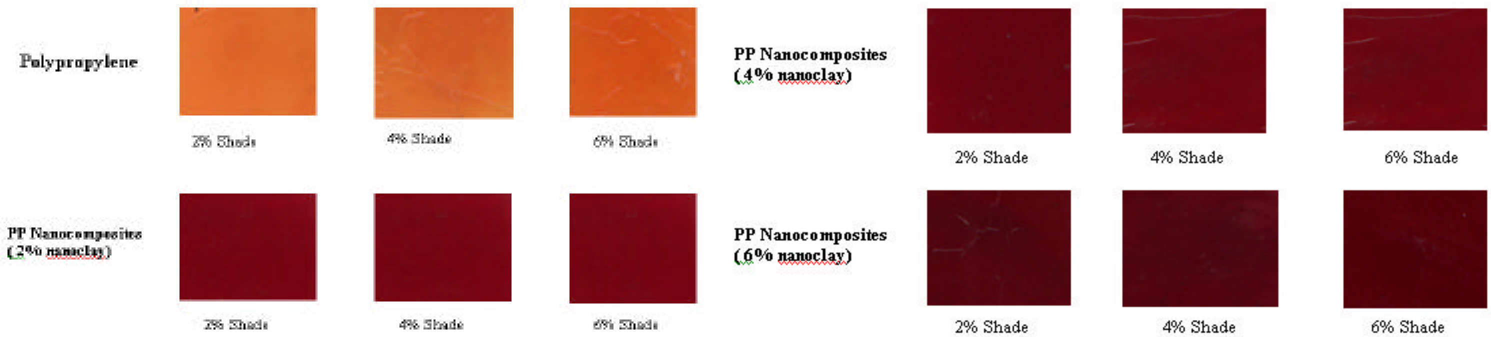

Figure 4 C.I. Acid Red 266 Dyed PP Nanocomposites

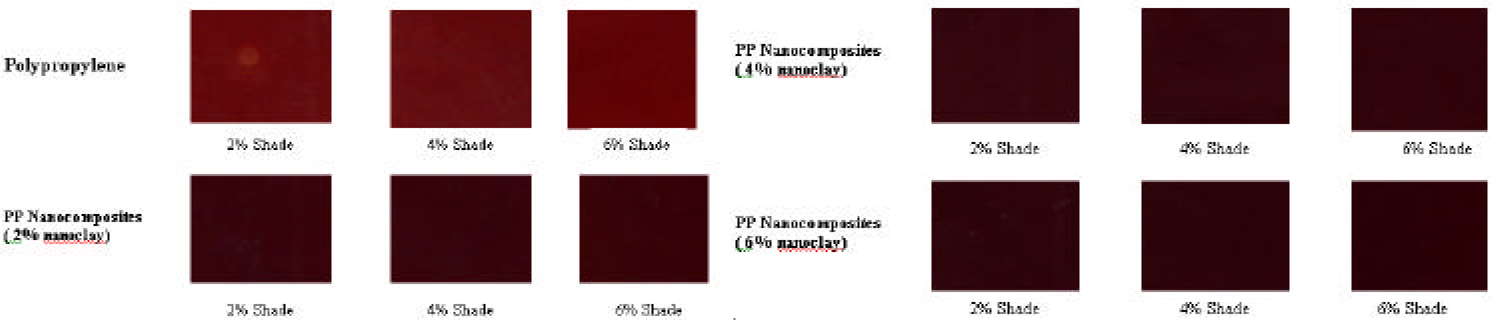

Figure 5 C.I. Disperse Red 65 Dyed PP Nanocomposites

Other types of nanoparticles, such as nano ZnO, nano Al_2O_3, nano SiO_2 and nano TiO_2 were also invested to determine their feasibilities in the research. Up to this moment, no good dyeing results were obtained.

Next Year's Goals:

1. To determine the distribution of nanoparticles in polypropylene;
2. To study the dyeing mechanism and to improve the dyeing levelness and colorfastness;
3. To prepare, dye, and characterize the fiber form of the PP nanocomposite;
4. To explore the chemical finishing of the dyeable PP nanocomposite fibers with regard to flame retardant, fluid repellent and antimicrobial properties.

Approach:

1. The TEM and XRD facilities at University of Nebraska Lincoln (UNL) together with FTIR, SEM, DSC and TGA at UMD will be used to characterize the distribution of nanoclay in the PP nanocomposites in both film and fiber formats. We will also study the morphological properties of the PP nanocomposite fibers.
2. Suitable dyestuffs for the PP nanocomposites will be selected with respect to their chemical structures, color fastnesses, and application methods. We propose to study the kinetics and the dyeing mechanisms operational at the acid dye-fiber and the disperse dye-fiber interfaces with the aid of computer modeling technology.
3. A Brabender extruder with appropriate fiber processing attachment will be used to produce the PP nanocomposite fibers. Characterization and dyeing of the resultant fibers will be conducted.
4. Chemical finishing technology will be used to improve the multi-functional properties of PP nanocomposites.

Outreach to Industry:

Contact has been made with the fiber producers, e.g., Equistar in Texas, and textile industry, e.g., Milliken in North Carolina. We plan to form partnership with two PP fiber producers and two PP textile manufacturers in order to obtain guidance and to develop industrial applicable technologies in fiber production and textile processing areas. A patent application is in progress. Several presentations have been given at conferences in the UK and the US.

New Resources Required:

A particle size analyzer, fiber forming attachment for the Brabender extruder and computer softwares are to be procured to facilitate the planned research activities for next year.