Pilot Demonstration of Technology for the Production of High Value Materials from the Ultra-Fine ($PM_{2.5}$) Fraction of Coal Combustion Ash

Semi-Annual Technical Progress Report

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Principal Authors: T. L. Robl, J. G. Groppo, Robert Rathbone

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Center for Applied Energy Research
University of Kentucky
Lexington, KY 40511

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Abstract

During this reporting period, efforts focused on improving our understanding of the basic operating principles of the lamella classifier. It was determined from testing that product grade is primarily a function of the classifier configuration and operation and the feed grade has relatively minor influence. Additionally, within the range of the testing conducted, the feed density did not seem to have an impact of the yield. Thus, the product composition will not be strongly influenced by the variability of the feed, an important consideration for heterogeneous ponded fly ash.

Three types of chemically and functionally different thermoplastic polymers have been chosen for evaluation with the fly ash derived filler: high density polyethylene, thermoplastic elastomer, and polyethylene terphthalate. The selections were based on volumes consumed in commercial and recycled products. The reference filler selected for comparison was 3 µm calcium carbonate, a material which is commonly used with all three types of polymers.

A procedure to prepare filled polymers has been developed and most (~80%) of the polymer/filler blends have been prepared. Selected samples of filled polymers were subjected to SEM analysis to verify that the fly ash derived filler and the calcium carbonate were well dispersed.

A stainless steel mold with cooling capabilities was built in-house to prepare 1 mm thick films for tensile strength and Dynamic Modulus testing. Procedures are being developed to insure a minimum of air voids in the films, which will eventually be evaluated for a variety of physical and mechanical properties.

Executive Summary

Project efforts focused on improving our understanding of the basic operating principles of the lamella classifier, a critical step for the conceptual design of the process demonstration unit. A basic conclusion that can be drawn from testing conducted during this reporting period is that product grade is primarily a function of the classifier configuration and operation and the feed grade has relatively minor influence. It can also be concluded that, within the range of the testing conducted, the feed density did not seem to have an impact on the yield. Testing was conducted at 5%, 12% and 15% feed solids at the 2 cm spacing and yields varied from ~9% for the 5% solids to ~10.5% at 15%. If particle-particle interaction resulting in hindered movement were a dominant factor, the yields would be reversed, i.e. higher for the less dense feed. Thus, the product composition will not be strongly influenced by the variability of the feed. This is important for ponded fly ash, which is a heterogeneous material.

Three types of chemically and functionally different thermoplastic polymers have been chosen for evaluation with the fly ash derived filler. The selections were based on volumes consumed in commercial and recycled products. The three thermoplastic polymers selected are:

- Dow HDPE DMDA-8907 NT 7 high density polyethylene (HDPE);
- Santoprene 55 thermoplastic elastomer (TPE); and
- Dupont Crystar 3946 polyethylene terphthalate (PET).

The reference filler selected for comparison was 3 µm calcium carbonate (Omya PW-3), a material which is commonly used with all three types of polymers.

A procedure to prepare filled polymers has been developed and most (~80%) of the polymer/filler blends have been prepared. Selected samples of filled polymers with 20% and 50% or 60% filler were subjected to SEM analysis to verify that the fly ash derived filler and the calcium carbonate were well dispersed.

Due to the high level of filler addition and number of tests required, a special stainless steel mold with cooling capabilities was built in-house to prepare 1 mm thick films for tensile strength and Dynamic Modulus testing. After minor modifications, several trials were conducted with the mold and procedures to insure a minimum of air voids is currently being developed. The following tests are planned over the next several months to evaluate the filled polymers:

- thermogravimetric analysis;
- scanning electron microscopy (pre and post failure);
- tensile strength & elongation;
- flexural strength;
- dynamic modulus analysis; and
- miscellaneous tests: impact strength and abrasion resistance.

Results and Discussion

The results and discussion of progress made during this reporting period are summarized in this section, which is organized by Task and Subtask. For clarity, major accomplishments of each Task or Subtask are highlighted with a narrative description of specific activities.

Task 1 – Feedstock Evaluation

The objectives of this task are to obtain the necessary data to finalize equipment selection for the PDU design and the reagent requirements to produce high quality filler and super pozzolan from both dry ESP ash and pond ash.

Subtask 1.1 Sample Procurement

Status: *Essentially Completed*

Subtask 1.2 Sample Characterization

Status: Essentially Completed

Subtask 1.3 Evaluation of Dispersion Parameters

This task is further divided into two subtasks.

Subtask 1.3.1 Evaluation of Flotation Parameters

Status: Essentially Completed

Subtask 1.3.2 Evaluation of Dispersion Parameters

Status: Essentially Completed

Subtask 1.4 Testing of Processing Parameters

This Subtask is divided further into three Subtasks

Subtask 1.4.1 Testing of Dispersion Parameters.

This activity is discussed under 1.5 below

Subtask 1.4.2 Testing of Dewatering

Previously Reported

Subtask 1.4.3 Environmental Testing

Subtask 1.5 Process Simulation.

Lamellae Classifier Testing.

The basic operating principles of the lamellae classifier, which was developed as part of this research, have been described in previous technical status reports. The overall yield and product grade are controlled by the residence time of the particles in the classifier, the superficial velocity of the flow (within specific bounds), the concentration of the dispersant, and the spacing of the lamellae. The latter parameters have been explored in previous research. The affect of lamellae spacing was investigated during this period.

The lamellae spacing has a control on the overall cut point of the particles by providing a surface to settle on. The settling velocity of properly deflocculated particles is controlled by Stokes' law, simply stated, $Vs=g D^2 (\sigma p- \sigma w)/18\mu$, where Vs is the settling velocity in cm/sec, g is the acceleration of gravity (980 cm/sec^2), D is the diameter of the particle in microns, σp is the particle density, σw is the density of water and μ is the kinematic viscosity. For example, given a 30 minute retention time and a vertical spacing of the lamellae of 2 cm, a 10 μm diameter ash particle would fall a total of 12 cm in the given retention time, thus all of the 10 μm ash material would be rejected. A 2 μm particle would only fall 0.5 cm in the same time and, theoretically, only 25% would be lost. In practice, very small particles, those below ~2 μm, significantly deviate from Stokes' law due to their very low mass and other forces, including Brownian movement, play a role.

Table 1 presents the parameters for the lamellae test series. Three spacings were investigated: 2, 4.4, and 7.2 cm. Three different dispersant dosages of the NSF (Handy Chemical Co.) were used for each trial. Retention time (~39 minutes) and superficial velocity (~4.1 cm/min) were held as constant as feasible for the tests.

Table 1. Parameters for Lamellae Spacing Tests.

Test	Lamellae Sp. (cm)	NSF g/kg	Feed Wt.%	Rt min	Sv cm/min
1	4.4	2.0	12.8%	38	4.2
2	4.4	2.50	12.9%	37	4.2
3	4.4	3.0	13.0%	40	3.9
4	7.2	2.0	13.8%	43	3.7
5	7.2	2.50	13.7%	38	4.1
6	7.2	3.0	13.9%	38	4.1
7	2.0	2.0	14.5%	38	4.2
8	2.0	2.5	14.6%	39	4.1
9	2.0	3.0	14.6%	39	4.1
10	2.0	2.0	11.8%	38	4.1
11	2.0	2.5	12.0%	37	4.2
12	2.0	3.0	12.3%	38	4.1
13	2.0	2.0	5.2%	37	4.3
14	2.0	2.5	5.3%	38	4.1
15	2.0	3.0	5.4%	39	4.0

Other parameters and results of the tests are presented in Table 2. The feed was held constant for most of the tests at ~14%, and the product yield was found to vary from 25% for the widest spacing to only 10% for the narrowest. Concomitant with the overall decrease in yield is an increase in grade, which improved from a D_{50} of ~ 3.8 µm to ~2.5 µm. The yield-grade curve for the various lamellae spacing is presented in Figure 1. Overall, the data appear to be congruent.

Table 2. Results of the Lamellae Spacing Tests.

Test	Lamellae cm	Feed wt%	5 µm Rec.	Product Yield	Feed D_{50} µm	Prod. D_{50} µm
1	4.4	13%	48%	15.7%	23	3.8
2	4.4	13%	69%	17.5%	28	3.2
3	4.4	13%	59%	18.3%	22	3.1
4	7.2	14%	51%	25.1%	11	3.8
5	7.2	14%	59%	25.5%	13	3.7
6	7.2	14%	52%	25.8%	11	3.6
7	2.0	15%	39%	10.3%	27	2.5
8	2.0	15%	47%	10.6%	29	2.4
9	2.0	15%	52%	10.5%	31	2.3
10	2.0	12%	48%	10.0%	27	2.6
11	2.0	12%	43%	10.5%	28	2.5
12	2.0	12%	35%	9.4%	23	2.5
13	2.0	5%	45%	9.1%	29	2.6
14	2.0	5%	38%	9.4%	24	2.5
15	2.0	5%	40%	8.7%	25	2.4

Several conclusions can be made from the tests. First, the overall grade of the product is primarily a function of the classifier configuration and operation. The tests for the 7.2 cm spacing used a much finer feed which did not seem to have an impact on the product grade-yield curve. Secondly, within the range of the tests, the feed density did not seem to have an impact on the yield. Test were run at 5%, 12%, and 15% feed solids at the 2 cm spacing and yields varied from ~9% for the 5% solids to ~10.5% at 15%. If particle-particle interaction resulting in hindered movement were a factor in the tests, the yields would be reversed, i.e. higher for the less dense feed. Thus, the product composition will not be strongly influenced by the variability of the feed. This is important for ponded fly ash, which is a heterogeneous material.

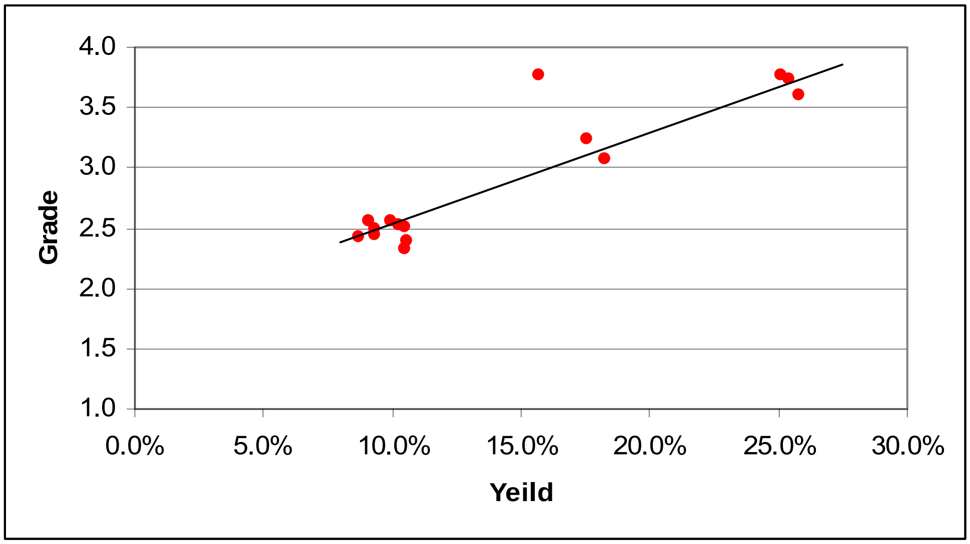

Figure 1. Yield vs. Grade plot for Varied Lamellae Spacing

Task 2. Pilot/Demonstration Plant Final Design.

Subtask 2.1 PDU Conceptual Design of PDU Facility

Status: Essentially Completed

Subtask 2.2 PDU Construction of PDU Facility

No activity this period.

Task 3. Pilot/Demonstration Plant Operation

No activity this period.

Task 4. Product Evaluations and Final Economic Evaluation

Subtask 4.1 Commercial Scale Final Design

No activity this period.

Subtask 4.2 Product Testing.

Subtask 4.2.1 Superpozzolan Testing

Status: Essentially Completed.

Subtask 4.2.1 Filler Testing

Preparation of Fly Ash Derived Filler

A very fine filler was prepared by processing ash from a utility fly ash pond with hydraulic classification system employing a novel combination of hydraulic and lamella classifiers. The fly ash was dewatered to 65 – 75% solids and then dried to a powder. The general properties of the filler from several classifier runs are as follows:

- D_{50}: 3 – 5 µm
- Specific gravity: ~2.41
- Loss on ignition: 2 – 3 %
- Carbon content: 1 – 2%
- Morphology: spherical
- Color: dark grey

Fly ash from additional sources will also be processed and evaluated as fillers in plastics, once a sufficient amount of material is recovered by processing.

Preparation of Filled Polymer Systems

Three types of chemically and functionally different thermoplastic polymers have been chosen for evaluation with the fly ash derived filler. The selected polymers are used in large volumes in commercial and recycled products, and therefore offer the greatest opportunity for utilization. The three thermoplastic polymers are:

- Dow HDPE DMDA-8907 NT 7 high density polyethylene (HDPE);
- Santoprene 55 thermoplastic elastomer (TPE); and
- Dupont Crystar 3946 polyethylene terphthalate (PET).

The latter plastic is a major component of municipal solid waste (MSW) which is recycled and blended with other plastics to manufacture post consumer (second tier) products such as industrial pallets, plastic lumber, etc. Due to the highly variable nature of MSW, virgin PET has been used in this program to represent MSW plastic. PET was also chosen because it contains ester groups and therefore should exhibit good bonding with the fly ash derived filler without the addition of coupling agents (see below). The reference filler selected for comparison was 3 µm calcium carbonate (Omya PW-3), a material which is commonly used with all three types of polymers.

Filled polymer systems have been prepared with a Haake PolyLab System (Rheomix 3000p) mixer using R3000 (roller-rotor) mixing blades. To prepare the samples, the mixer was first heated to a temperature which is 5°C above the melting or softening point of the polymer, and then the polymer was added with the mixer operating at 20 rpm. After approximately 10 minutes of mixing, the filler was introduced into the melt over a 30 – 60 second period. The total mixing time has ranged between 25 and 70 minutes depending on the polymer and filler type. Generally, mixing was terminated 15 to 20 minutes after the torque reading from the mixer has reached a minimum (after filler addition) and was stable. After cooling, the melt was ground into particles which are typically less than 6 mm in size. The ground polymer will be used to prepare films for testing, as described below.

Table 3 summarizes the combinations of polymers and fillers and filler loading levels which will be prepared for the test program. All of the HDPE and TPE with fly ash or calcium carbonate fillers have been prepared and ground. Fifty percent of the polyethylene terphthalate/fly ash blends have been prepared and ground; calcium carbonate filled blends remain to be prepared. Overall, ~80% of the polymer/filler blends have been prepared and ground

Table 3. Filler Test Program: Materials and Proportions

Polymer Type	Filler	Part by Weight
High Density Polyethylene	Ghent	0, 10, 15, 20, 40 & 60
	Mill Creek	
	EWB	
	Trimble	
	$CaCO_3$	
Thermoplastic Elastomer	Ghent	12, 20, 35, 50 & 65
	Mill Creek	
	EWB	
	Trimble	
	$CaCO_3$	
Polyethylene Terphthalate	Ghent	0, 10, 20, 40 & 60
	Mill Creek	
	EWB	
	Trimble	
	$CaCO_3$	

Selected samples of filled polymers with 20% and 50% or 60% filler were subjected to SEM analysis to determine the level of dispersion of the filler (see Figures 2, 3 and 4). Initial results indicate that the fly ash derived filler and the calcium carbonate were well dispersed. Preliminary TGA data is available for the first set of samples (i.e., polymer filled systems) submitted, but additional samples have been submitted and the data is pending (results will be reported at a later date).

Due to the high level of filler addition and number of tests required, a special stainless steel mold with cooling capabilities was built in-house to prepare 1 mm thick films for tensile strength and Dynamic Modulus testing (Figures 5 and 6). After minor modifications, several trials were conducted with the mold. Procedures to insure a minimum of air voids is currently being developed.

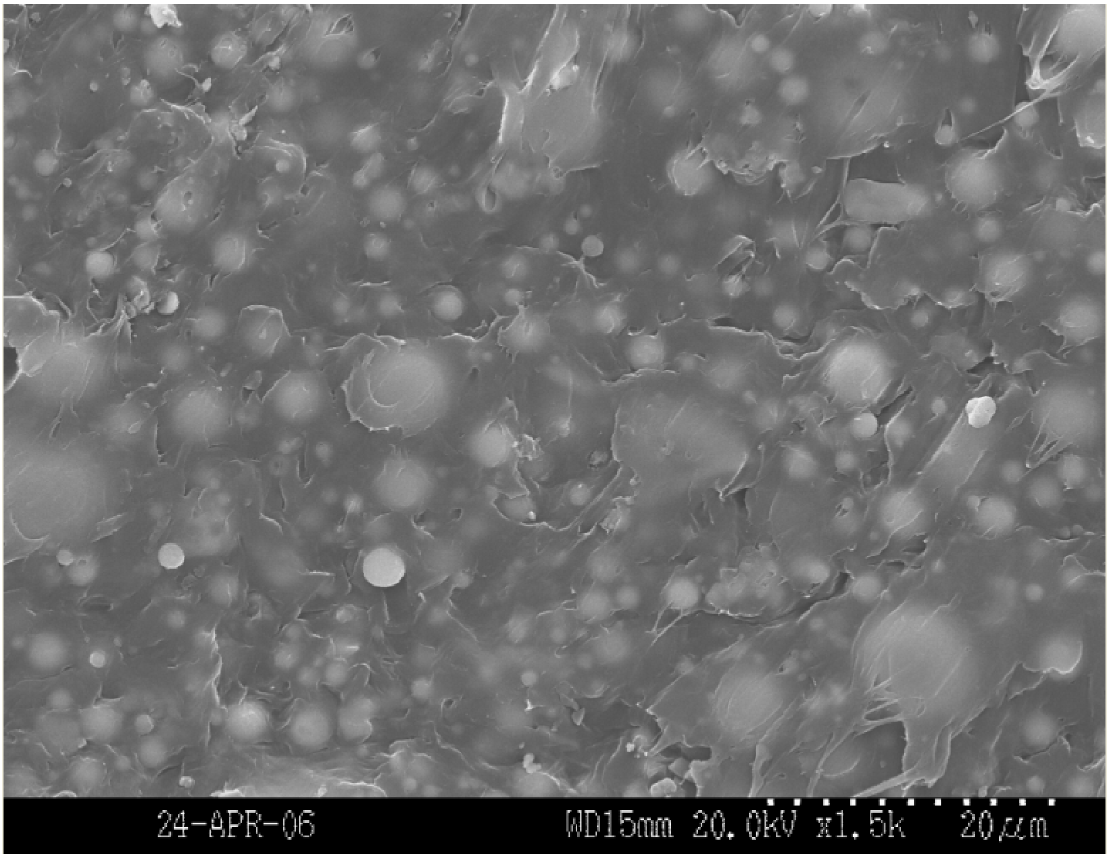

Figure 2. 60% Fly Ash in HDPE

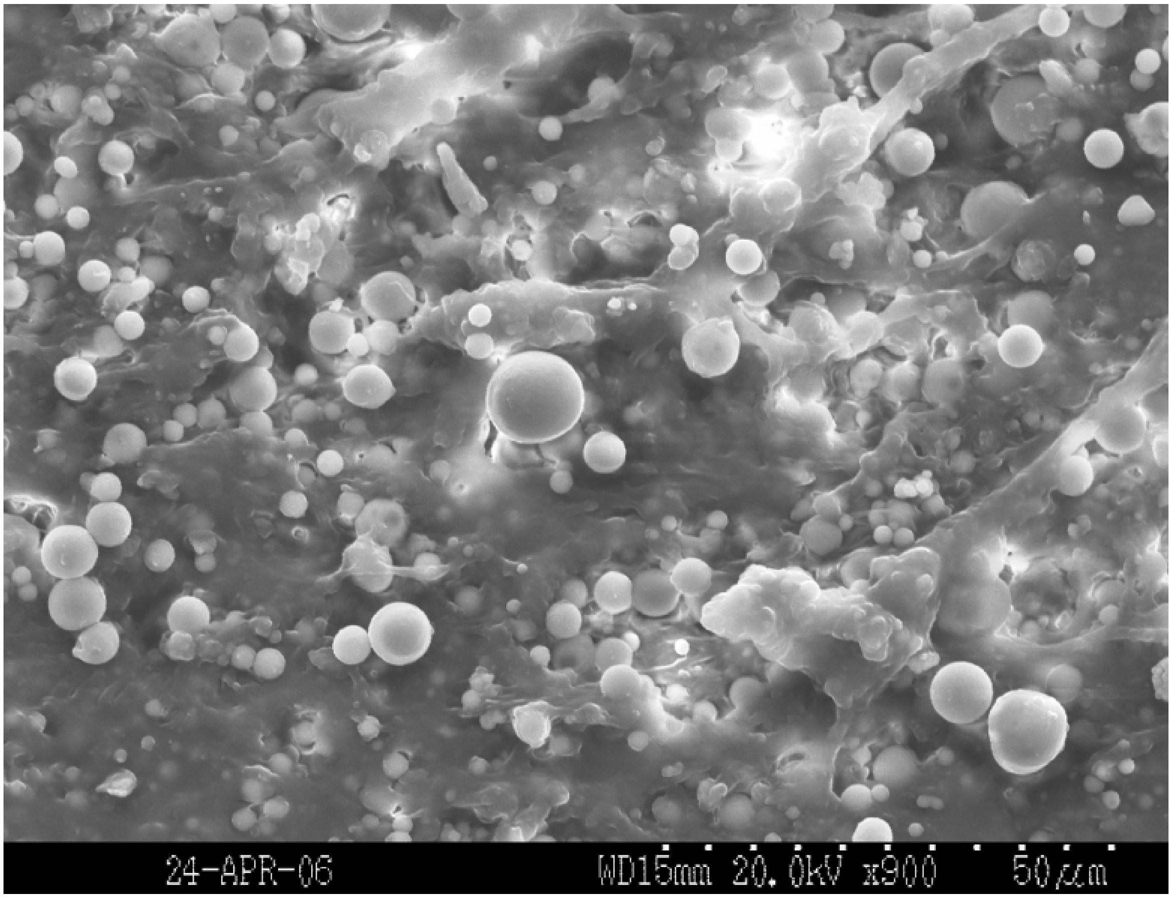

Figure 3. 50% Fly Ash in Santoprene (TPE)

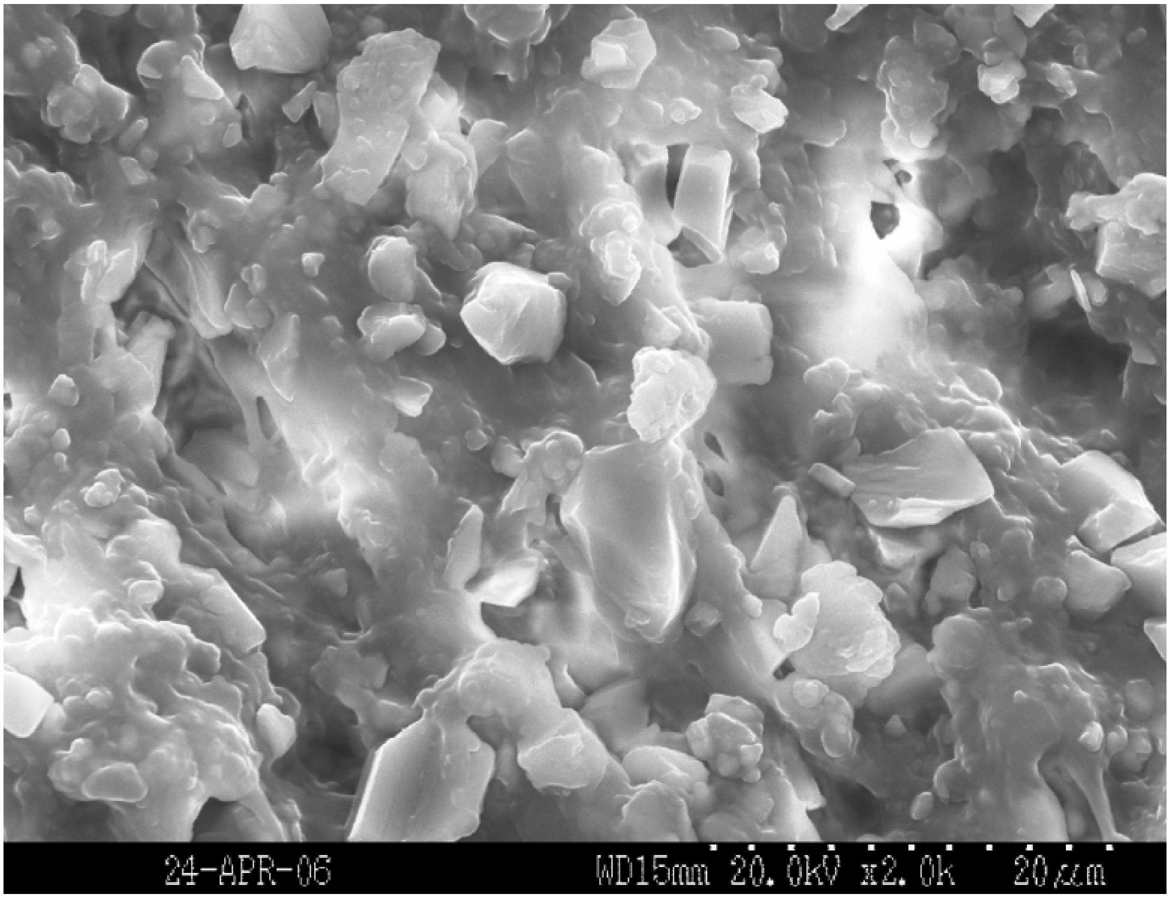

Figure 4. 50% Calcium Carbonate in Santoprene

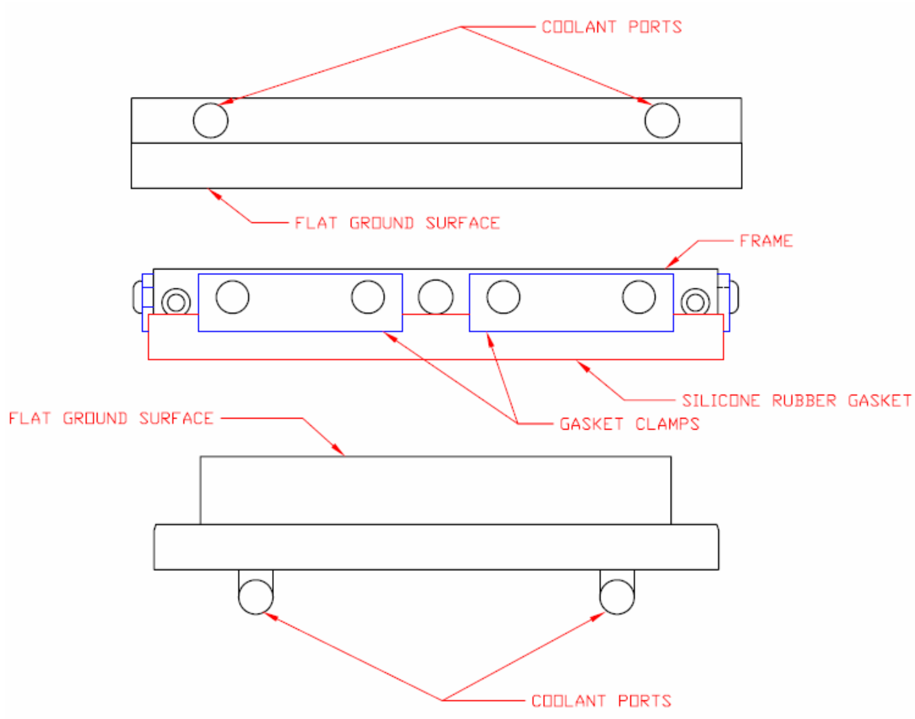

Figure 5. Stainless Steel Mold for 1 mm Thick Films

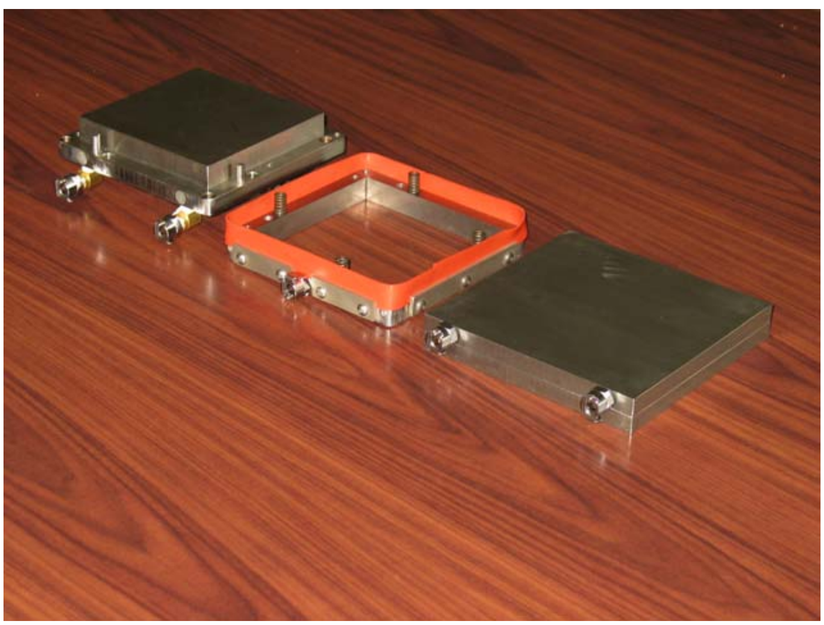

Figure 6. Photograph of Stainless Steel Mold for 1 mm Thick Films

Evaluation of Physical Properties of Filled Plastics

The following tests are planned over the next several months to evaluate the filled polymers:

- thermogravimetric analysis;
- scanning electron microscopy (pre and post failure);
- tensile strength & elongation;
- flexural strength;
- dynamic modulus analysis; and
- miscellaneous tests: impact strength and abrasion resistance.

As previously mentioned, all prepared samples will be tested by thermogravimetric analysis (TGA) to confirm the content of the filler. Scanning electron microscopy (SEM) will be used before to confirm that the filler is well dispersed in the polymer before additional physical tests are performed. The tensile strength and elongation properties of the unfilled and filled polymer systems will be obtained by preparing 1 x 133 x 133 mm film sheets and cutting appropriate sized "dogbone" shaped samples.

Dynamic Mechanical analysis (DMA) will yield information on the viscoelastic properties of filled polymer systems such as the loss modulus (viscous component) and the storage modulus (elastic component); the glass transition temperature (Tg) will also be obtained with this method.

Coupling Agents

The compatibility of the fly ash derived and calcium carbonate fillers with HDPE and TPE will be improved through the use of titanate and silane based coupling agents, which chemically react with the filler surface and lower its surface energy. Typically these additives allow significantly higher filler loadings without increasing melt viscosity, and improve tensile and flexural strength.

A modified ASTM D 281 (Oil Absorption of Pigments by Spatula Rub-out) method has been used to determine the optimum level of titanate for the fly ash derived filler. Inconclusive results have been obtained to date because the method of application (of the additive to the filler) affects the results. Additional work is required to determine the optimum level of coupling agent.