FINAL TECHNICAL REPORT

Project Title: Accelerated Characterization of Polymer Properties

Covering Period: June 19, 2001 through June 19, 2003

Date of Report: July 18, 2003

Recipient: GE Global Research
PO Box 8
Schenectady, NY 12301

Award Number: DE-FC07-01ID14093

Subcontractors: Cytec Industries, K-Tron International, Inc.

Other Partners:

Contact(s):   R. Wroczynski, Principal Investigator
GE Global Research
1 Research Circle
Niskayuna, NY 12309
518-387-6674, e-mail: wroczynski@crd.ge.com

Co-authors: L. Brewer
D. Buckley
M. Burrell
R. Potyrailo

Project Team: DOE-HQ contact: Dickson Ozokwelu
Project Manager: Joel Trent

DISCLAIMER

"This report was prepared as an account of work sponsored by the the United States Department of Energy. Neither the United States Government nor the Department of Energy, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the Department of Energy thereof. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the United States Government or the Department of Energy."

Executive Summary

This report describes the efforts to develop a suite of microanalysis techniques that can rapidly measure a variety of polymer properties of industrial importance, including thermal, photo-oxidative, and color stability; as well as ductility, viscosity, and mechanical and antistatic properties. Additional goals of the project were to direct the development of these techniques toward simultaneous measurements of multiple polymer samples of small size in real time using non-destructive and/or parallel or rapid sequential measurements, to develop microcompounding techniques for preparing polymers with additives, and to demonstrate that samples prepared in the microcompounder could be analyzed directly or used in rapid off-line measurements. These enabling technologies are the crucial precursors to the development of high-throughput screening (HTS) methodologies for the polymer additives industry whereby the rate of development of new additives and polymer formulations can be greatly accelerated.

The polymer properties that were the primary focus of this investigation were downselected using the Quality Function Deployment (QFD) process to those that would most benefit from HTS techniques. These properties were identified as functional groups, oxidative stability, color and color change, ductility, and tensile strength along with molecular weight and viscosity. Our efforts focused on developing microanalysis analysis techniques for these properties primarily using polypropylene with stabilizers as the test system. In addition, micro techniques for rapidly measuring the anti-static properties of polymer formulations were also developed.

A wide array of mechanical, spectroscopic, and chemical methods were explored for measurement of the identified properties. Many methods showed promise for further development into robust high throughput microanalysis methods. Among these are:

- correlation of stabilizer effectiveness in polypropylene with on-line or in-line fluorescence spectroscopy, with microcompounder torque changes, and with dynamic melt behavior of extruded pellets
- parallel measurement of weathering in polycarbonate with an acoustic wave transducer system
- measurements of yield stress and modulus via micro or nano indentation
- measurements of ductility using a novel, micro-scale, auto-feed film, biaxial impact device
- rapid, automated measurements of static decay on plastic films using a novel, spot charger/electrostatic voltmeter device
- correlation of low to medium liquid/melt viscosities of polymers with the force required to move the liquid in an automated liquid handling probe.

However, in many cases significant additional optimization of the techniques will be required for the particular polymer and/or additive systems being explored. For example, the mechanisms of degradation differ across polymer systems. Chain scission or branching or both may occur for different types of polymers resulting in the need to tune the selected instruments to the polymer system. In a similar manner, the chemical natures of the different additives can show different levels of interference with spectroscopic methods and the system will need to be optimized to minimize that interference while maximizing the measured response. This is not atypical of what is currently done with traditional instruments and measuring techniques.

In addition, some of the methods that show promise require the use of films. The microcompounder used in this program has only a limited capability of making film and a compounding system with a wider processing capability is needed to supply film of sufficient width, thickness, and consistency to be used in the methods that utilize films.

The microcompounder, when coupled with micro loss-in-weight, computer-controlled feeders, was demonstrated to be capable of creating gradient compositional arrays which could be used in on-line or off-line rapid analyses for UV weathering or melt flow (degradation) studies.

A candidate set of potential customers were contacted and asked to participate in a survey to clarify the design needs for commercial device(s) identified in this program. Although a relatively low response rate of less than 14% was obtained, the participants did represent the most important market segments. The low response to the survey appeared to be due to at least in part to concerns about disclosure of proprietary information. The results of the instrument needs survey indicated that an automated, flexible, co-rotating twin screw extruder with multiple feed devices and relatively low throughput rates coupled with an integrated laboratory management system is desired. This device would also be coupled with microanalysis capabilities for on-line melt rheological, color, composition, and morphological dispersion measurements. Physical, thermal, dynamic mechanical, mechanical, and chemical were mentioned as properties appropriate for off-line microanalysis. Survey participants placed a high premium on increased productivity, targeting from two- to ten-fold increases in throughput.

The commercialization plan for a Combinatorial Microcompounding/High Throughput Screening Product Development platform is organized to consist of three phases ultimately resulting in a three-tier product offering. These product tiers are:
1.   Polymer/Additive Systems (Tier 1)
2.   Polymer/Polymer Systems (Tier 2)
3.   Reactive Compounded Systems (Tier 3)

The first tier development, which deals only with polymer/additive systems, was directly addressed by this program. Tiers 2 and 3 involve more complex polymer systems requiring more demanding compounding equipment and additional analysis methods beyond those addressed by this program. The development of Tier 2 and Tier 3 product development platforms will follow the realization of the Tier 1 offering.

Based on the results of the microanalytical methods development and the customer needs mapping, a preliminary design specification was written for a Microcompounding High Throughput Screening Product Development Platform (CSS). The device will consist of an extruder, feed system, computer control and data collection system with various in-line and off-line analysis systems.

TABLE OF CONTENTS

TABLE OF TABLES

TABLE OF FIGURES

Project Objective

The primary objective of this project was to develop a suite of microanalysis techniques for rapid evaluation of polymer formulations. The microanalysis methods were directed toward:

- Simultaneous analyses of multiple polymer samples of small size in real time.
- Where possible, development of nondestructive measurements that could allow multiple analyses to be made on the same library of samples.
- Increases in overall analysis speed.
- Developing the enabling technology for the development of a combinatorial or high throughput experimentation methodology that could greatly accelerate the rate of development of new additives technology

Background

Additives are an essential and often expensive part of many polymer formulations. They play a crucial role in new materials development imparting enhanced or new performance properties. Suppliers are constantly seeking improvements in processing and higher output of finished products with an ever more sophisticated range of properties. However, current polymer test methods are slow, labor intensive, and require consumption of large quantities of test materials. As a result, the introduction of new additives technology is extremely slow and costly. Traditional additive packages are often utilized without revalidation for new applications, or further development is terminated once a moderate level of performance is achieved resulting in over- or under-engineered performance. The development of new microscale, rapid tests for polymer properties will enable a significant acceleration in the rate of new additives and plastics development, open up new materials applications through increased polymer performance and decreased cost of polymer development and manufacturing, and reduce energy consumption and waste production associated with disposal of poor performing or off-specification materials.

Accomplishments

Task 1—Downselect Key Properties for Microanalysis

A broad range of additive types are used to impart an equally large set of properties to polymers (**Table 1**). Our first action in this program was to downselect from the large array of polymer properties to those properties that had the broadest impact across a range of additives and would have the most impact in speeding up additives development by utlizing a high throughput methodology.

The project partners (GE and Cytec) worked together over a series of face-to-face and teleconference meetings using Six Sigma tools to identify the key performance properties of stabilizer systems that would benefit most strongly from High Throughput Screening (HTS) techniques. The first step involved discussions which led to importance rankings of groups of properties for plastics performance, the polymer types (i.e., engineering resins, polyolefins, styrenics, PVC, etc), and stress conditions (weathering, thermal aging, processing, etc) on which to focus further analysis. With these rankings in hand, a QFD (Quality Function Deployment) process [1] was employed to describe the relationships between the polymers in

specified stress conditions and performance properties and to identify areas to focus HTS methods development.

Table 1. Classes and functions of additives.

Additive	Function
Stabilizers (thermal, oxidative, UV, etc.)	Provide protection from degradation in process or in use.
Plasticizers	Reduce stiffness, impart flexibility, and improve processability.
Lubricants, flow aids	Improve processability, reduce wear.
Fillers	Impart stiffness, structural integrity.
Flame retardants	Reduce tendency to ignite or propagate combustion.
Impact modifiers	Improve ductility.
Compatibilizers, coupling agents	Improve compatibility in blends of polymers or fillers.
Colorants	Aesthetics.
Conductivity modifier	Impart conductivity or antistatic properties.
Antifungal, antimicrobial	Provide protection from biological attack.

The results of this process are depicted in **Figures 1** and **2**. The team had determined that the important target areas were those listed in the far left column of House 1 (e.g., polyolefin resin weathering, engineering resin weathering, etc). The effects that various material changes listed in the top row had on the various target areas are depicted by h(igh) and m(edium) in the intersection boxes (an empty box indicates a low or no effect). Tallying of the total effects for a particular material change gives the relative importance of that change across the target areas.

Figure 1. QFD House 1. Material changes that influence key target areas.

Target Areas vs Matl Change

Material Change

Target Area	Importance	Oxidation	Chain scission	By-product formation	Cross-linking	Rearrangement	Unsaturation formation	Morphological		Total
Olefin Weathering	5	h	h	m	m		m	m		150
Engineering Resin Weathering	4	h	m	h	m	h	m			144
Olefin Process Degradation	3	h	h	m	h		m	m		108
Olefin Thermal Aging	3	h	h	m	m		m	m		90
Engineering Resin Process Degradation	2	m	m	h	m	h	m	h		78
Total		141	117	87	69	54	51	51		

In House 2 (**Figure 2**), the team defined how particular polymer properties were able to measure the material changes. In addition, the degree of difference that is needed to be determined between values of a given polymer property to determine a significant material

change is shown in the "Targets and Specs" row. With this QFD, it was then possible to establish which polymer properties were of the most importance in terms of influencing the target areas. The first five polymer properties listed (functional groups, oxidative stability, color & color change, ductility, and tensile strength & tenacity) have a strong correlation with most of the target areas. In addition, molecular weight and viscosity are seen to also have a strong correlation with more than 50% of the target areas. Therefore, our efforts have subsequently focused in developing HTS methods primarily in these areas for polymer stabilization with most of the initial activity focused in the polyolefins stabilization area.

Figure 2. QFD House 2. Polymer properties that measure material changes.

Matl Change vs Polym Props

Polymer Properties

Material Change	Importance	Functional Groups (POOH, >C=O, Nitroxide, >=<)	Oxidative stability	Color and Color Change	Ductility	Tensile strength, tenacity	Chemical resistance	MW	Tm	MWD	Viscosity	Odor	Hardness	Haze	Gloss	X-link density	Permeability	Solubility parameter	Tg	Stiffness	Crystallinity	Total
Oxidation	5	h	h		h		m	m	m				m	m		m	m	m				285
Chain scission	4	h	m		h	h	h	h	h	h	h	m	m		m	m		m	m	m		384
By-product formation	3	h	h	h				m				h		m								126
Cross-linking	2		m			h	h	m		h	m	h	h			h			m	m	m	162
Morphological	2				h	m	m	m		h			m	h	h		h		m	m	h	138
Rearrangement	2	m		m			m						m							m		36
Unsaturation formation	2	h	h	h			m									m	m	m				78
Total		132	108	96	87	75	75	63	60	54	54	54	51	48	45	45	39	39	36	24	24	

Targets and Specs: Failure1 @ Δw% >C=O = 0.1% (PP) & 0.5% (PE). Measurement capability =+/- 0.01% (ca 10% rel). OIT and O2 uptake. O2 considered more relevant. Capabili ca 10% relative. Failure ΔE = 3. ΔYI = 5.Measurement error (ΔE) 20% relative. ΔE) = 0.5 significant. NI Failure: PC ductile ==> brittle. 20-30% change significant. Dynatup depends on material. 20% Δ significant. Failure1 @ 50%Δ. Early indicatoir1 @ 30%Δ. Requires 5-1 samples. Film s/v ca 3-5%. % Failure vs time in strain1/g w exposure. 50%Δ considered significant. Large errors. Customer specific. Typically not used much vs MWD. Typically not used. For narrow MWD 10% relative significant. PE MFR 20%Δ significant. Food pkg, qualitative. Some literature on microindentation but not used routinely except for coatings. 3-5 unit change considered significant. Failure 50% of original value. 10%Δ considereed significan. For rubber: 20% difference significant.

Only one additional area has been explored beyond what was indicated in the QFD, that of dielectric properties, in particular, anti-static performance. This area entails some unique performance properties that are not covered by the stabilization target areas and not covered by the general physical property categories such as ductility and tensile strength. So this polymer property area was added for a slight expansion in scope.

Task 2—Develop Advanced Micromeasurement Techniques for Polymer Properties

Task 2.1—Develop techniques for measurement of chemical properties.

A range of microanalysis tools for analysis of chemical properties were developed that enable the monitoring of early stages of thermooxidation reactions. The chemical parameters of interest were selected from the results of our analysis of customer CTQs as detailed in Task 1. During polymer processing, numerous chemical reactions occur in the polymer backbone that change the chemical composition of polymers. In particular, in polyolefins, these reactions include radical attacks and recombinations, exothermic fragmentations, rearrangements, and electron transfers. These reactions lead to variation in molecular weight of polymers, generation of low molecular weight colored products, rdeuction in melt flow index (MFI), and generation of volatiles. All of these changes were found to be important to customers. The tools investigated during the project for microanalysis of chemical properties of polymers include spectroscopic, chemoluminescence (CL) imaging, and various sensors as summarized in **Table 2**. These microanalysis tools preserve the rank order of performance yet enable monitoring of early stages of thermooxidation reactions and lead to acceleration in analysis speed.

Table 2. Microanalytical tools for analysis of chemical properties of polymers.

Customer parameter	Microanalysis Approach	Comments
MFI (related to molecular weight of polymer)	• In line and at line spectroscopy • Torque change during compounding • Extruded pellet melting behavior	Demonstrated for conventional and/or micro-scale extruders.
Peroxide groups	Chemoluminescence imaging	Demonstrated for samples from conventional and micro-scale extruders.
Volatiles during polymer processing	Metal oxide semiconductor sensors	Demonstrated for samples from conventional extruders.
Extractables	Acoustic wave sensors	Applied on samples from conventional extruders.
Weathering performance of thin polymer films	Acoustic wave transducers	Demonstrated for polycarbonate thin films.
Solubility or chemical resistance	Acoustic wave transducers	Demonstrated for array of polycarbonate copolymers.
Viscosity	Delivery force in liquid handler	Demonstrated for series of PDMS fluids. Potential use for polymer melts for stability or polymerization kinetics evaluations.

These techniques were refined from known detection principles or were developed from new detection schemes to meet the need for a particular application. For efficient operation of

the HTS systems across several uses in this project, an infrastructure was developed. Combinatorial samples were analyzed for different properties of interest by either serial or parallel measurements using in situ or post-reaction sampling. The measurements were performed using a variety of modular spectroscopic equipment and different types of transducer arrays [2-4]. A unifying theme across the components of this infrastructure is a common platform for data acquisition, network communication between experimental stations, and data management. Details of the selection of a proper measurement and sampling approaches and strategies for development of new high-throughput screening tools are detailed elsewhere [5].

In-line and at-line spectroscopic determinations of MFI

A methodology was developed for rapidly screening changes in MFI during polymer processing of polypropylene compositions. This method employed the use of spectroscopic measurement techniques. While the behavior of polymers under thermal and UV degradation has been studied by IR and Raman, these methods are relatively insensitive requiring hundreds of hours of polymer exposure. Thus, the disadvantages of applications of vibrational spectroscopic techniques are their low sensitivity toward small changes in MFI and other polymer properties during extrusion.

Fluorescence analysis of polymers, including polypropylene has been reported in the past where the fluorescence signature of polypropylene was correlated with a single performance parameter. It was shown that the extent of photodegradation is the greatest with polypropylene samples showing the highest initial intensity of fluorescent emission, demonstrating that the impurities responsible for fluorescence participate in photodegradation [6]. Possible sources of fluorescence with excitation in the region 230-260 nm were shown to be conjugated CO groups in the polypropylene chain [7]. Changes in fluorescence caused by thermal degradation have been reported [8]. It was shown that the initial fluorescence of the polymers is caused by the presence of α,β-unsaturated carbonyl compounds. In addition to causing fluorescence, these structures also accelerate thermal degradation. It has been concluded that post-oxidative fluorescence is caused by short polyene sequences which may or may not be conjugated to carbonyl groups [9].

In our method, fluorescence spectroscopy is coupled with the application of multivariate analysis methods to simultaneously quantify MFI and color of polypropylene during processing (see Task 2.2, Multivariate Methods for Simultaneous Analysis of Color and MFI). Advantages of the developed method over known approaches for fluorescence analysis of polypropylene include: simultaneous quantitation of several performance parameters of polypropylene using fluorescence, application of multivariate methods for analysis of fluorescence data of polypropylene degradation, capability for analyzing polymer samples in situ during polymer processing, increase in analysis speed by using an automated high throughput analysis spectroscopic station, and capability for multiple testing and analysis steps of different polymer properties on the same library of samples in a nondestructive fashion. These advantages can accelerate the identification of new additive formulations for polymers and can enable examination of broader range of polymer additive formulations.

Validation details are provided in Task 3 along with a discussion of some of the issues discovered with this technique and their potential solutions.

Torque change during compounding

The use of in-line and on-line melt rheometers has been extensively explored as a way of monitoring the melt viscosity or melt index of polymers during the extrusion process. [10]. However, the extremely small size of our microcompounder hinders the use of many of these approaches, since such devices are often larger than the microextruder alone. Previous studies have often had the objective of obtaining the true melt viscosity in order to avoid traditional methods such as capillary rheometry. We are only interested in obtaining relative rank ordering that can match those obtained with traditional MFI results. Traditional studies of melt process stabilizer effectiveness in polymers have often employed extended mixing times in batch mixers. Variations in the mixing torque in these mixers have been correlated with process stability[11]. The microcompounder also has the capability for monitoring the screw torque during processing [12]. We explored this measurement for estimating degradation-induced MFI shift of a series of stabilized PP materials.

The screw torque in the microcompounder is estimated from the current drawn on the DC drive motor. The torque is proportional to the current and voltage controls the drive speed. The manufacturer set the output of the torque value so that the maximum motor torque allowed (6 N-m) corresponds to a current draw of 2 A [12].

Figure 3. MFI vs microcompounder torque for PP.
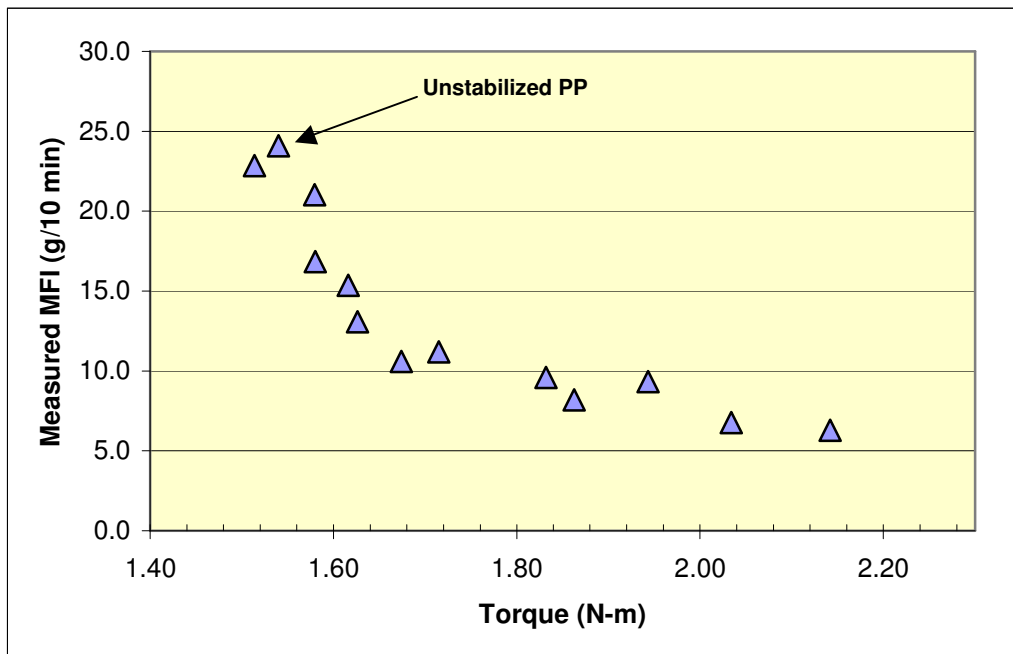
Figure 3 shows the relationship of the MFI's measured for various stabilized PP compositions after extrusion in the microcompounder under abusive conditions (see Task 4.2 for details) with the average torques measured for these compositions during extrusion. There

is a strong correlation of the torque with the measured MFI with the unstabilized material showing a large MFI and lower torque. Additional validation details are provided in the Task 3 section.

Extruded pellet melting behavior

During the course of working with PP pellets extruded in the microcompounder we noticed that materials with different MFI appeared to melt very differently. The pellets of less degraded materials with lower MFI's showed a marked tendency to shrink and retract while the more degraded materials with higher MFI appeared to spread away from the initial elongated pellet shape as shown in **Figure 4**. It is known that, upon extrusion through an orifice, polymers undergo an elastic response, die swell [13], and that thermal degradation of PP results in a lower MW, narrower MW distribution, and less die swell [14]. The differences observed in the melting behavior of the PP pellets could be related to differences in the amount and rate of the recoverable shear strain induced in the extrusion process and quenched in the water bath. Upon melting of the pellets, the materials resume the elastic recovery process. Since the rate and amount of recoverable strain are both dependent upon MW and MW distribution of a given polymer [14, 15], the melt behavior we observe should also correlate with the MFI. [16]

Figure 4. Changes in pellet shape on melting. Numbers correspond to MFI measured for the pellets below. Examples of initial pellet shapes are shown at the bottom.
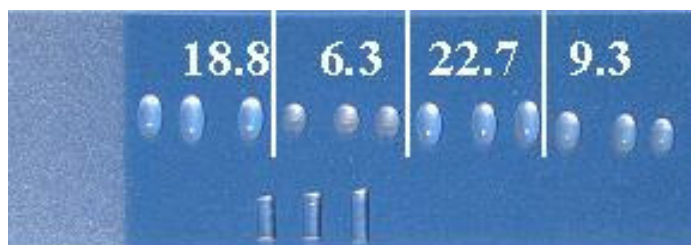
The relationship of the melt behavior with the MFI of the material was tested using the measurement of changes in pellet length before and after melting and determining the correlation with the MFI measured for the corresponding sample of pellets. This method, coupled with an automated image analysis system for measuring the dimensional change offers potential for use as a primary screen to identify the most promising stabilizer systems and additional validation details are given in the section on Task 3.

Determination of thermooxidative stability of materials arrays using chemiluminescence imaging

Exposure of polymers to varying environmental conditions during polymer production and life cycle leads to changes in a variety of chemical properties of polymers. A variety of reactions such as self-recombination of secondary peroxy radicals and others provide chemoluminescence from the thermo- and photo-oxidized polymer [17, 18]. A system was developed that includes a high-sensitivity and low noise imaging detector to monitor

chemoluminescence with a previously unavailable level of sensitivity and spatial resolution. We selected a CCD camera with a high quantum efficiency in the spectral range of interest, low dark noise due to sufficient cooling, and high spatial resolution. These capabilities only recently became available on the market.

Validation details are provided in Task 3.

Determination of oxidative stability of polymers using chemical sensors

Determination of volatiles in polymers is another important aspect of the evaluation of polymer stability. At the polymer-processing stage, the sources of emitted volatiles typically include degradative reactions under the effects of heat and shear, additives used during polymer manufacturing, and reactive volatile diluents in thermoset formulations [19]. These and other volatile-emission sources produce a variety of volatile organic compounds (VOCs) such as residual monomers, volatile contaminants, moisture, solvents, decomposition products of thermoplastics, decomposition products of additives, actual additives, and some others [19]. Volatiles emitted during end-use originate from polymer degradation due to thermal, ultraviolet, and other types of environmental exposures [20, 21].

Because of the importance of the evaluation of volatiles during polymer processing, a variety of analytical techniques has been used. For example, analysis of volatiles from processing of polyolefins has been performed using IR gas analysis, colorimetric detection, gas chromatography and mass spectrometry [19]. Principal volatiles from polyolefins include carbon monoxide, formaldehyde, acrolein, and some others at parts per million concentrations [19]. Unfortunately, these techniques suffer from being labor intensive in sample preparation and from having bulky instrumentation. Overall, these techniques are not particularly suitable for rapid at-line determination of volatiles during polymer processing. Thus, we evaluated the use of chemical sensors that have a suite of features that make them attractive for applications ranging from health care and diagnostics, to environmental and process monitoring, and to monitoring of terrorist activities and military applications [22, 23]. The sensor features that are attractive for these and many other applications include portability of instrumentation, no need for costly carrier gases, high sensitivity of analysis, capability to provide real-time information about composition and concentrations of volatiles, and relatively low cost [24-27]. Because individual sensors often do not respond to a single analyte but to a class of vapors due to their cross-sensitivity, selective analyte detection in complex mixtures can be achieved by using several sensors with diverse sensor films and analyzing the response pattern of such a sensor array by means of different pattern recognition techniques [23,28,29].

In our evaluations, we applied a metal oxide semiconductor (MOS) chemical sensor array for determination of amounts of volatiles produced during multiple extrusions of polypropylene [30]. The speed and sensitivity of analysis are important parameters for development of analytical instruments for high-throughput screening of materials. Because acoustic wave sensors provide the most sensitive response toward volatile analytes [25,26,31,32], these sensors were initially evaluated for analysis of volatiles from extruded polymers. The sensors used in this study were previously described in detail [31]. Briefly, they were AT-cut quartz crystals oscillating in the thickness-shear mode with a fundamental frequency of 10 MHz and coated with acoustically thin polymer films for detection of polar and nonpolar vapors. However, the response and recovery of acoustic-wave devices operating at

room temperature was significantly slower than MOS sensors as illustrated in **Figure 5**. Thus, MOS sensors were selected for further analysis.

Figure 5.   Comparison of response and recovery times of (A) acoustic wave and (B) MOS sensors upon exposure to degradation products. Regions: 1, vapor pulse containing degradation products; 2, air, 30%RH; 3, dry nitrogen gas.
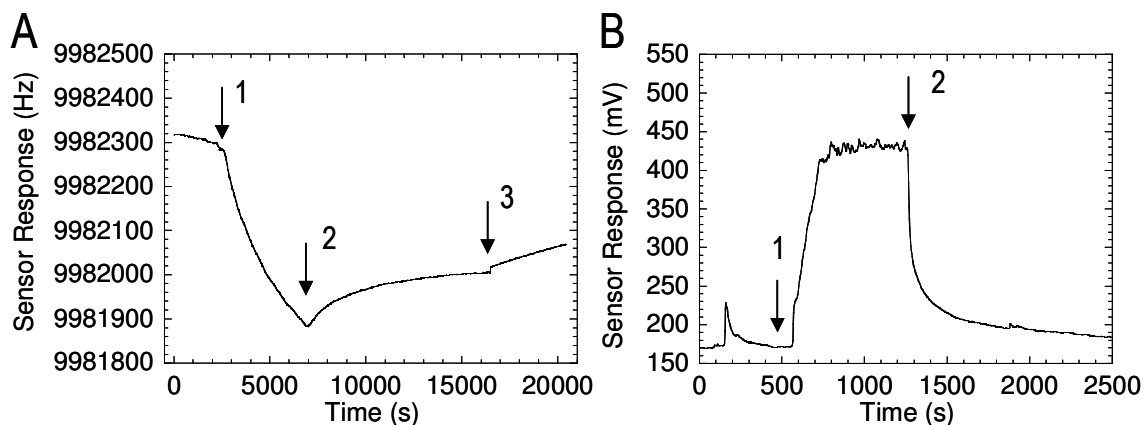
Figure 6. Sensor array performance upon exposure to six samples of degraded polymer formulation B. (A) Kinetic sensor responses for implementation in the PCA. Scores plot of PC1 vs PC2 (B) and PC2 vs PC3 (C) of the kinetic sensor responses.
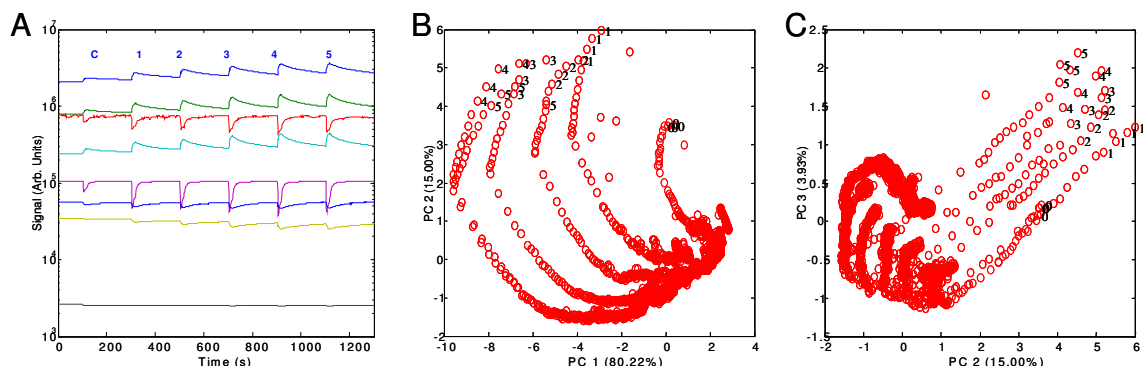
To take into the account the responses of all sensors in the array, the response of the array was analyzed using multivariate analysis tools that provide a suitable pattern recognition approach. The pattern recognition goal was to find similarities and differences between chemical samples based on measurements made on the samples. Methods of pattern recognition include principal components analysis (PCA), hierarchical cluster analysis, soft independent modeling of class analogies, neural networks, and others [33, 34]. We selected PCA because of its simplicity and ease of application for analysis of dynamic data. Principal components analysis is a multivariate data analysis tool that projects the data set onto a

subspace of lower dimensionality with removed collinearity [35]. PCA achieves this objective by explaining the variance of the data in terms of the weighted sums of the original variables with no significant loss of information. These weighted sums of the original variables are called principal components (PCs). For this analysis, we used responses from eight out of ten sensors, sensors 2 and 8 induced a considerable noise into the PCA analysis and were ignored. Responses of the remaining eight sensors and scores plots are presented in **Figure 6**. This data demonstrates that three PCs can adequately describe the kinetic response of the sensor array to various volatile samples. The first three PCs accounted for more than 95% variance captured by PCA. This data demonstrates that PCA differentiates concentration-dependent dynamic responses of the sensor array toward volatiles from differently degraded materials.

To determine relative amounts of volatiles generated during polymer processing, we analyzed sensor responses from three samples of a polymer degraded to different extents as described by their MFI range from 4.5 g/10min (essentially unchanged) to 26.2 g/10min (degraded). The sensor signals from all polymers are summarized in **Figure 7A**. This figure

Figure 7. Quantitative analysis of polymer degradation with the sensor array. (A) Summary of sensor response to polymer grades 1 – 3 after compounding and multiple extrusion passes. (B) MFI for all studied polymers. Numbers 1 - 3 are polymer grades where 1 is the least stabilized and 3 is the most stabilized.
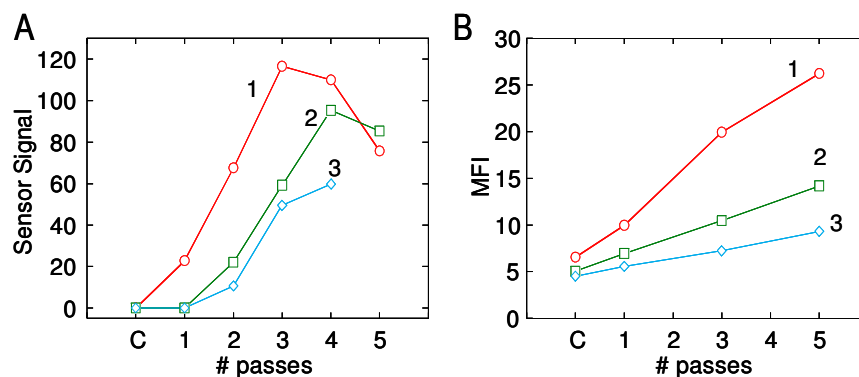
demonstrates that indeed more degraded polymers produce more volatiles at 1 – 5 pass processing. For the technique to be applicable for materials ranking, it should correlate with a conventional analysis method such as MFI. The correlation between sensor signal and MFI for all studied polymers is demonstrated in **Figure 7B**. The amount of detected volatiles after the fourth extruson pass decreased and the rank ordering of polymers was distorted. Thus, a good correlation of rank order of detected material degradation between traditional and sensor-based measurement was obtained over mild degradation conditions, up to the fourth extrusion pass.

This study demonstrated that the use of sensor arrays could provide quantitative information about polymer oxidative stability and can be an attractive alternative to a gas chromatography for the rapid evaluation of a large number of samples. It can be applied to the evaluation of polymer oxidative stability after multiple-pass extrusions or single-pass extrusions under more severe conditions [36] and can viable for a rapid ranking of oxidative stability of polymer formulations. While this approach for detection of volatiles seemed to work, we decided to stop this effort because the polymer ranking based on MFI could be also obtained

using other developed techniques (See **Table 2**). In particular, spectroscopic and chemiluminescence (CL) detection methods were also promising and required less sample and fewer sample preparation steps.

The detection of volatiles from samples heated after compounding (thermally oxidatively degraded) was also explored using the same array of MOS sensors. The end of a ¼" piece of Cu tubing was positioned 1mm from the sample in order to detect volatile species liberated from plastic samples which were heated using a homebuilt gradient heater assembly. A small diaphram pump was added to the exhaust side to introduce volatile species into the sensor array. Control experiments were performed by heating an empty sample holder and monitoring the detector response.

Figure 8 shows the evolution of volatile species during three separate heating experiments (heating to 200°C, 250°C, and 300°C). The experiment starts (time = 0) with an empty sample holder under the Cu tube. After 100 seconds, the empty sample holder is slid to the side and a second pan with unstabilized PP (already at temperature) was placed under the sampling tube. At time ~200 seconds, the unstabilized PP sample was moved to the side of the heater – no sample is present and after 300 seconds, a third pan with a preheated stabilized PP sample was placed under the tube. This sequence was repeated three times to see if the data

Figure 8. Monitoring the degradation of stabilized and unstabilized PP.

are reproducible.
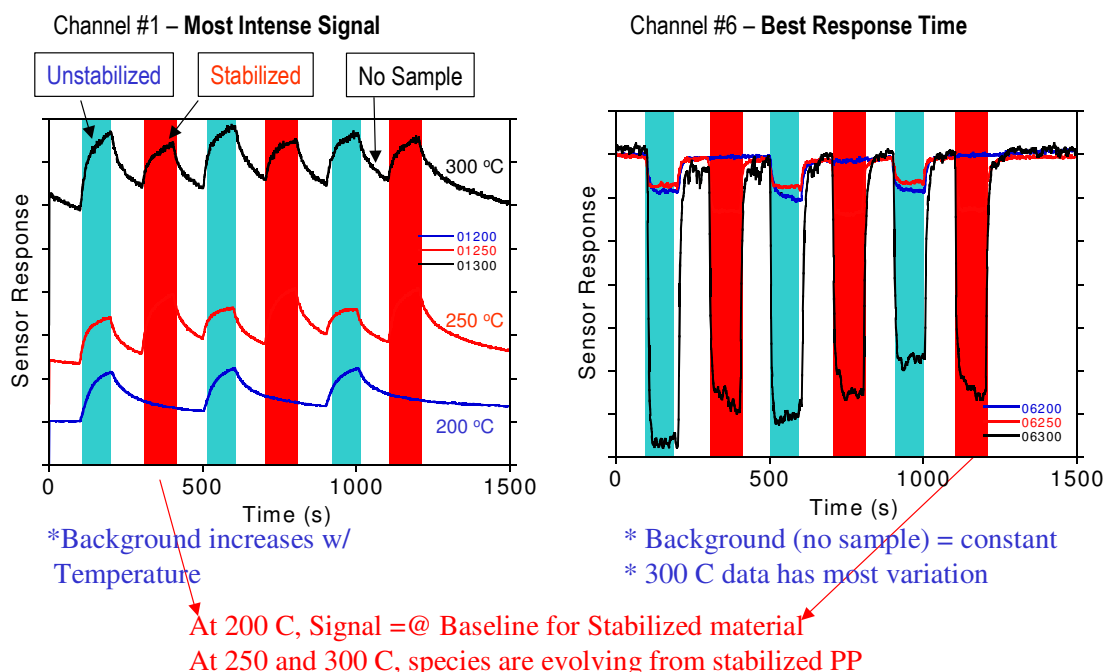
The left panel of **Figure 8** shows channel 1 response – these traces have not been offset. Channel 1 showed the most intense signal upon heating. Important observations for channel 1:

- Volatile species are detected from the unstabilized PP sample after heating to 200° C.
- Volatile species are not detected when the stabilized PP sample was heated to 200° C.
- The signal intensities continued to increase with increasing time (e.g. after 100 seconds, the signals were still increasing).
- Upon heating, the background intensity increased rather significantly.
- Upon heating to 250° C, volatile species are detected for both unstabilized and stabilized PP samples.

The right panel of **Figure 8** shows data collected from channel 6.   Channel 6 had the best response time, additionally for this channel, the background remained constant as the temperature changed.   Important observations for channel 6 are:

- At 200° C, volatile species are not detected for stabilized PP.
- As the temperature increases, the amount of volatile species liberated from the stabilized PP sample increases.   The amount of volatile species liberated from the unstabilized sample was similar at 200° C and 250° C.   The quantity increased significantly upon heating to 300° C.
- Repeat sampling of the same material revealed a different quantity of volatile species (data are not reproducible) – indicating that these measurements are time/temperature sensitive.

Although a characteristic signal for the different samples can be detected, quantification of the response requires very good control of the temperature and time at temperature. However, measurements performed on PP samples with different MFI values did not reveal a correlation between detector response and MFI (amount of degradation).

It is important to point out that with the any sensor array, one measures a change in detector response, however the sensor array does not identify the species responsible for the response (eg. CO being liberated). The sensor array detection may not be able to differentiate different processes – such as desorption vs. decomposition if similar species are generated during different processes.

In order to positively identify the species responsible for change in detector response, a detector with higher chemical selectivity is needed such as a mass spectrometer (MS) or a gas chromatograph. With a MS, a spectrum of the volatile species can be monitored such that one can directly identify the volatile species.   Mass spectrometers capable of unit mass resolution, a mass range of ~500 amu, and capable of operating under ambient conditions are offered by a few vendors. Mass spectrometers with higher mass resolution and higher mass range are also available – these commercial instruments have not been used for ambient analysis yet. An Inficon Transpector CPM 0-100 amu quadrupole mass spectrometer was tested. Gas sampling was performed using a glass capillary that was terminated using a stainless steel Cajun VCR fitting that had a similar size as the sample holder. The VCR fitting was placed ~1mm above the sample.   The sample heater used for the MOS sensor measurements above was also used for this analysis.   Upon heating from 200° to 300° C, numerous volatile species left the sample and were detected. The response time of the detector was very rapid, similar to the response time of Channel 6 of the sensor array . These initial experiments showed that mass spectrometry is a viable technique for detecting volatile species leaving PP during heating but quantification for this technique also is sensitive to accurate control of temperature and time at temperature. This route was not pursued further due to the relatively high cost of the instrumentation.

Determination of weathering performance and solubility of polymers using an acoustic-wave transducer array

For rapid evaluation of viscoelastic, vapor-sorption, solubility, and other properties of polymeric materials fabricated using high-throughput and combinatorial chemistry methods, we developed a 24-channel acoustic-wave transducer system. The system is based on thickness-shear mode (TSM) acoustic-wave transducers. We used the AT-cut piezoelectric quartz crystals previously described in detail [32] and outlined in Task 2.1, Determination of Oxidative Stability of Polymers Using Chemical Sensors. For evaluation of polymer properties, the crystals were coated with the polymer films of interest. Depending on the screening needs, the polymer films were then exposed to different testing conditions. Examples of these conditions include temperature, humidity, and a variety of organic solvent vapors. Alternatively, the approach used for solubility (chemical resistance) of polymers was to expose an array of polymers in an array of solvents and then over time expose clean crystals to the polymer-solvent mixtures. An oscillating electrical field was applied to the electrodes of each crystal using individual low-noise 4 – 22 MHz oscillators. Upon exposure of the coated crystals to the environment of interest, the frequency of oscillation of the coated crystals varied [37]. The fundamental oscillation frequency was monitored with a frequency resolution better than 0.01 Hz.

Validation details are provided in Task 3.

Figure 9. Strain gages on liquid handler syringe for measuring viscosity.
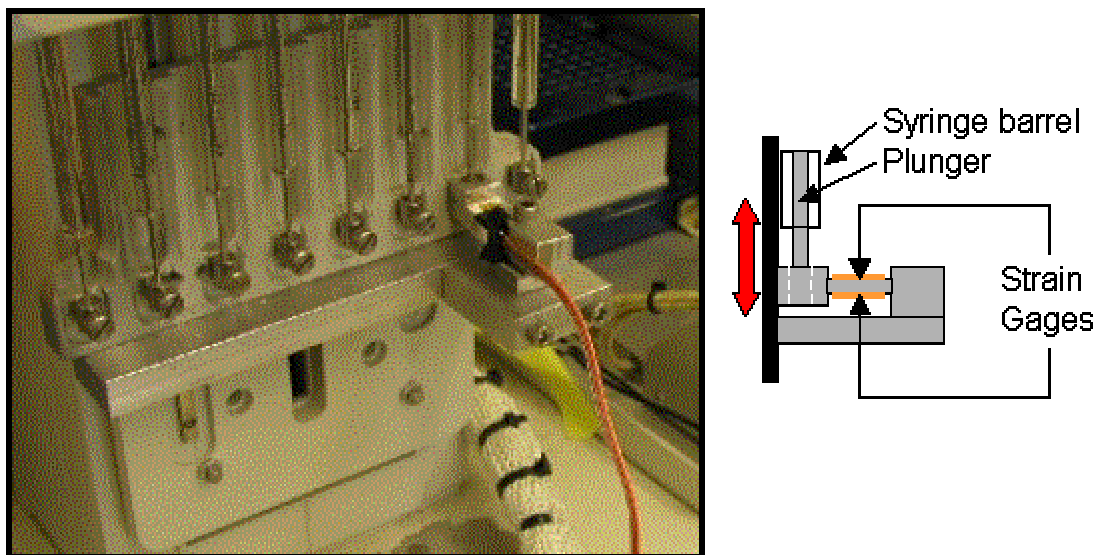
Determination of relative melt viscosity of polymers using an automated liquid handler

The melt viscosity of polymers is measured for a variety of reasons: to obtain an indication of the processability of the polymer, to estimate the degree of conversion during polymerization, or to determine changes resulting effects of environmental or process conditions. In addition to the extensive work already discussed concerning measurement of

MFI, we investigated a method of measuring the melt viscosity of low molecular weight polymers that could be used without compounding and during or immediately after polymerization. The concept involves aspirating material into a syringe probe of a liquid handler and then measuring the force to withdraw (push) the material back out of the probe into the vessel. With proper heat control of the probe and vessel, this method could be used for polymers that are liquid above ambient temperature.

Since this work was initiated late in the program, we have only achieved a proof of concept stage. This effort used polydimethyl silicone (PDMS) fluids of varying viscosities. A Gilson 215 liquid handler with 1.1 mm ID probe was used. Strain gages were attached to an aluminum arm (**Figure 9**) which was attached to the syringe piston and the driving arm. The voltages that were generated as the strain gages deformed during the piston movement were recorded versus time throughout the aspiration and withdrawal cycles of the fluids. The peak force (measured in mV) to initiate movement of the PDMS fluids out of the probe were found to

Figure 10. Relationship of strain gage peak dispense voltage vs measured MFI for PDMS fluids.

PDMS Viscosity vs mV Strain Gage Dispense Force

$y = 912.49x - 9713.7$
$R^2 = 0.9978$
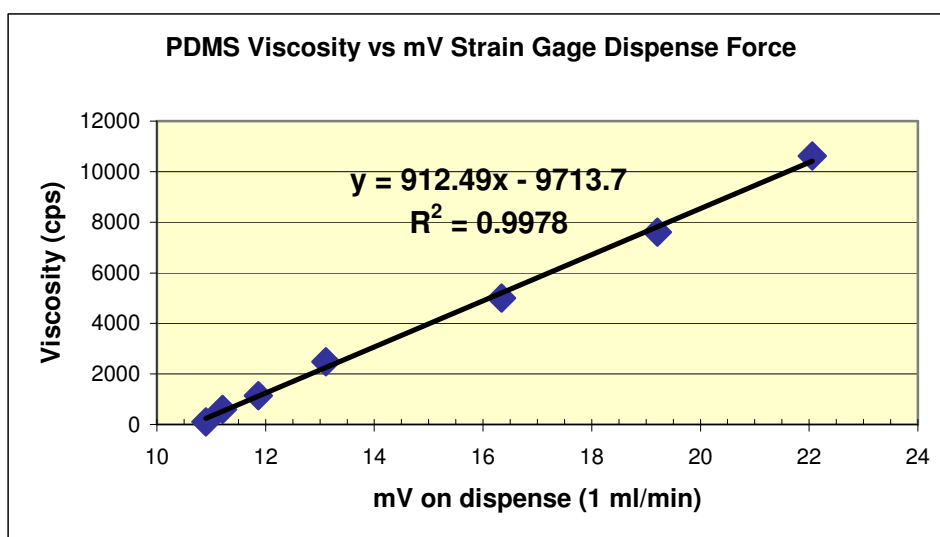
correlate well with the measured viscosities of the fluids (**Figure 10**). This method, with additional validation and refinement could have potential for measuring low to medium viscosities of small quantities (0.5-1.0 g) of materials.

Task 2.2—Develop techniques for measurement of optical and dielectric properties.

A range of microanalysis tools for measurement of optical and dielectric properties of processed polymers were developed. During polymer processing, numerous chemical reactions occur in the polymer backbone that change not only the chemical composition of polymers, but also vary the amounts of highly colored degradation products. The tools developed for the microanalysis of optical and dielectric properties include spectroscopic and static dissipation measurement methods as summarized in **Table 3**. These tools preserve the rank order of additive performance yet enable monitoring of early stages of thermooxidation

reactions and lead to acceleration in analysis speed. A summary of the developed microanalysis techniques is provided below.

Table 3. Microanalytical tools developed for analysis of optical and dielectric properties of polymers.

Customer parameter	Microanalysis Approach	Comments
Color	In-line and at-line spectroscopy	Demonstrated on conventional and micro-scale extruders with off-line and in line analysis.
Static dissipation	Micro-scale corona charging and electrostatic voltmeter measurement	Demonstrated for PE, PC/ABS and PC.

Multivariate methods for simultaneous analysis of color and MFI

During polymer processing, degradation products constitute one of the main sources for the discoloration of polypropylene [20]. It is known that these colored species have luminescence quantum yields which are sufficient for their emission detection [6,7]. Fluorescence detection is more sensitive than color analysis [38] and is useful for determination of low amounts of degradation products undetectable by color analysis.

In the method that we developed, fluorescence spectroscopy is coupled with the application of multivariate analysis methods to simultaneously quantify color (as yellowness index, YI) and MFI of polypropylene during multiple processing steps (see Task 2.1, Multivariate Methods for Simultaneous Analysis of Color and MFI). This analysis is performed in a nondestructive, noncontact fashion. This analysis method is adaptable for high throughput screening when coupled to an available automated screening station. Validation details are provided in Task 3.

Static dissipation measurements

Static electricity can build up on plastics at several stages of manufacture, from powder to pellet to extruded or injection molded parts. It originates from triboelectric charging (friction) upon separation of the mold or contact with other parts, from streaming currents in the melt, or other sources of charge separation [39-44]. Its occurrence can cause problems ranging from safety (electric discharge or even explosion), to handling issues such as sticking to other parts or to the mold. Some applications of plastics such as electronics packaging, computer housings, etc. require the ability to dissipate static charge. Minimization of dust attraction is required in applications such as compact disks, which are often coated with metal or spin-coated layers requiring a smooth finish. Conductive particles, fillers, and chemical additives are often included in the formulation to provide the plastic with the required electrical characteristics, which can range over many orders of magnitude, as summarized in **Table 4**. In the current program, purely conductive materials are not likely to be encountered simply by combinations of additives in polymers. Static dissipative materials can be produced by the addition of certain

"antistatic" agents that alone or through the adsorption of a moisture layer render the surface conductive.

Table 4. Classification of materials by resistivity.

Materials Parameter	Resistivity (ohms/square)
Conductive	$<10^5$
Static dissipative materials	$10^5 – 10^{12}$
Insulator	$> 10^{12}$

The ability of the material to dissipate static charge is related to the surface and bulk resistivity values. A material with a lower resistivity will dissipate charge at a faster rate. However, the transfer function relating resistivity to static decay is not defined well enough to allow prediction of the static decay time curve from a simple resistance measurement. For example, the simplest model suggests that an induced surface voltage should decay exponentially with time as governed by the RC time characteristics of the material:

$$V= V_0 \exp \{-t/RC\} \qquad \textbf{(1)}$$

In practice, the time versus voltage curves are more complex and can rarely be modeled by a simple exponential decay [39-42]. In addition, the actual static decay behavior may depend upon environmental conditions such as humidity, or the migration of certain additives to the surface during molding or extrusion. Thus, it is not sufficient to measure only surface or bulk resistivity in order to evaluate static dissipative properties. An empirical method is to introduce a charge onto the surface of the plastic, and directly monitor the surface voltage as a function of time as the charge is dissipated to the contacting electrical ground. We have explored this type of measurement, while evaluating its adaptability to screening multiple samples in either an off-line or on-line configuration, in quantities (sample dimensions) likely to be produced by the combinatorial extruder or injection molding apparatus.

Two methods have been employed to introduce a surface charge onto plastics: a directly connected DC electrode, and a corona discharge positioned in the vicinity of the sample surface. In one method (see **Figure 11**), a non-contacting electrostatic voltmeter (or field meter) is positioned to measure the surface potential, and a contacting electrode is biased at a high

Figure 11. Surface charge dissipation measurement using contacting electrodes.
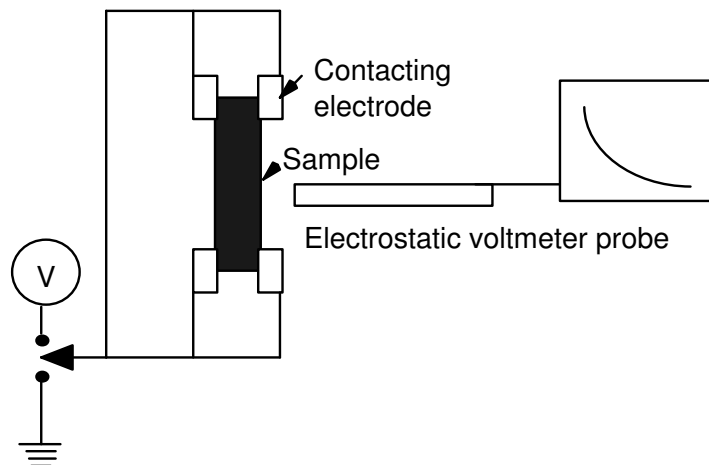
negative or positive voltage (usually ±5000V) until a stable surface charge is obtained at the position of the measuring electrode. At time t_0, the external voltage source is switched to ground potential, and the decay of the surface voltage is observed. This is the basis of Federal Test Method Standard 101B, Method 4046 [40].

      Our initial experimental set-up consisted of an external DC power supply, an electrostatic voltmeter (ESVM) and probe, a storage oscilloscope to monitor the output of the ESVM, and a pair of copper ring electrodes clamped to the top and bottom surface of the sample. Samples tested included PC/ABS blends containing an anti-static agent (obtained from GE Plastics, Selkirk NY); pink polyethylene bag material used to package circuit boards; polycarbonate (PC) plaques containing two types of anti-static agents (obtained from GE Plastics, Bergen op Zoom, Netherlands); Lexan® 8010 polycarbonate film (containing no anti-static agents), and assorted compact disks.   For the PC/ABS samples, the materials were known to have surface resistivities in the range of 10^{10} –10^{12} ohms/square and static decay times of less than 1 second. The surface voltage was observed to track the applied voltage, and then decay to zero as soon as the applied voltage was switched to ground. Voltage oscillations due to the mechanical switch noise prevented decay time measurements less than a few hundred milliseconds. A similar result was obtained for the pink polyethylene material. PC plaques containing anti-static agents, and conventional PC film, exhibited a different type of behavior, namely, the voltage measured at the plaque surface did not track the applied voltage, presumably due to their higher resistivity values (ca. 10^{12}-10^{15}), and their inability to conduct charge onto the surface. An alternative method to charge the polymer surface was tested, using a hand-held "Zero-stat" gun that contains a mechanical piezoelectric and a discharge point. Normally, this device is used to nullify the surface charge on plastics by emitting alternating bursts of positive and negative charges (by ionizing the air). In our experiments, it was found that the net charge deposited onto the sample surface could be somewhat controlled by squeezing the trigger in one direction only while pointed at the sample, then pointing the gun away from the sample while releasing the trigger. By using the output of the electrostatic voltmeter to trigger the storage oscilloscope, the static decay behavior of a variety of samples could be measured. **Figure 12** shows some typical results, and illustrates that the time frame of the static decay varied significantly from a few hundred milliseconds, to several hundred

Figure 12. Static decay measurements for PC (left) and anti-stat PC/ABS (right).
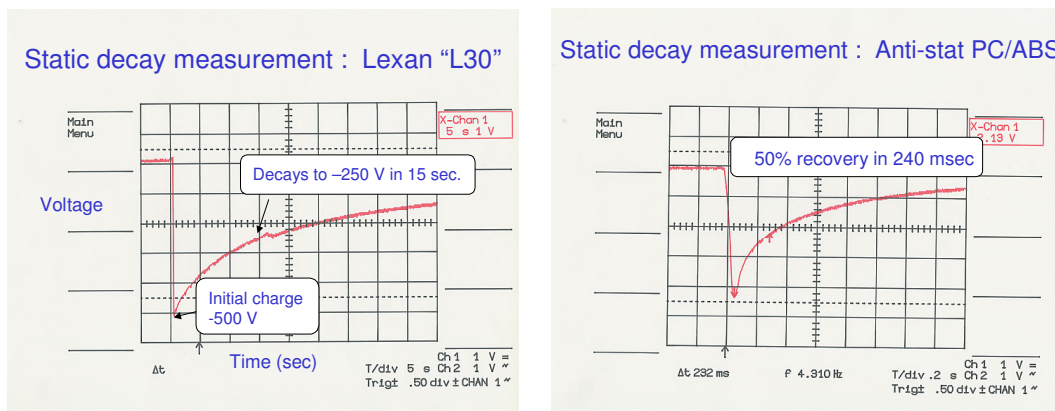
seconds or longer. Thus, it was determined that the static charge applied from the discharge source (rather than a contacting electrode) was applicable for a wider range of polymer formulations.

A method using a corona discharge as the charging source has been described in the literature [39-42], and is also employed in one commercial instrument used for measuring static decay characteristics [45]. Since the sample must be moved between the charging position and the measurement position, this method is relevant for measurement of static decay in the timeframe of seconds to minutes. In a more advanced setup, we incorporated a "spot charger" (manufactured by Julie Industries, Model PNV10) as a source of external static charge. Each sample of interest is moved first beneath the corona electrode for about 10 seconds to charge the surface, then positioned under the electrostatic voltmeter probe, to begin the measurement of the voltage versus time (static decay). Using this apparatus, we have measured the static decay behavior of a series of polycarbonate materials in different physical shapes and containing different quantities of anti-static additives.

Figure 13 shows the measured static decay curves for polycarbonate ribbon containing

Figure 13. Static decay curves for PC formulated with and without anti-stat additive.
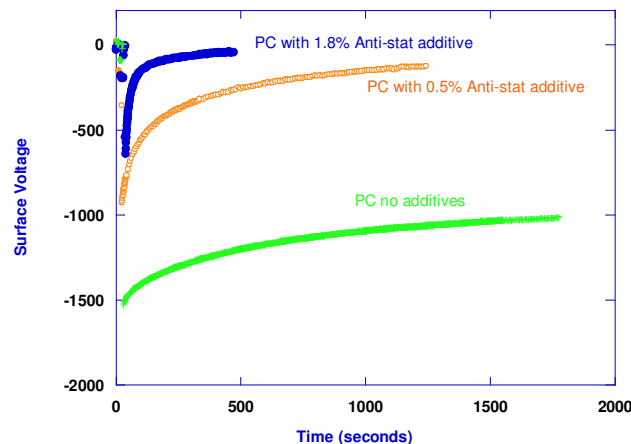
0, 0.5%, and 1.8% of an anti-stat additive. The improved dissipation of the static charge afforded by the additive is evident, as well as the ability of the system to distinguish between the sample types. Note also that the absolute magnitude of the initial charge is significantly different between the samples.

With the positive results obtained in these series of experiments, we proceeded to evaluating a more advanced setup and additional validation tests which are described in Task 3.

Task 2.3—Develop techniques for measurements of mechanical properties.

Four techniques were investigated and evaluated for determination of mechanical properties in polymers. Techniques were considered for evaluation based on the use of small quantities of material (1-10 g per sample) and the potential for high throughput relative to conventional test methods. The techniques chosen were: 1) thermographic analysis, 2)

miniaturized biaxial mechanical testing, 3) indentation testing, and 4) ultrasonic imaging. Most significant progress was made using techniques (2) and (3). Extensive experimentation using technique (1) illuminated the limitations of this method, and exploration of technique (4) was limited by issues with obtaining a suitable high temperature probe for use with the microcompounder.

Thermographic analysis

In theory, thermographic analysis should provide a rapid method of evaluating plastic deformation in polymers, using relatively small amounts of material. Work dating as early as 1943 indicates that released heat can be detected for a wide range of polymeric materials, including fibers and films [46, 47]. More recent work has examined thermal emission in toughened polymers [48, 49] and composites [50]. During deformation of a polymer past its yield point, heat is emitted, which reflects a temperature rise associated with bond breakage and rearrangement of polymer chains within the material. The total heat emitted from yield to final failure may be related to the ductility or elongation to break of the material.

Thermographic images of polymers under deformation were obtained in two configurations, uniaxial tensile and biaxial stretching using films of polycarbonate, polyetherimide, polypropylene and ABS. In uniaxial tension, multiple films were pulled in parallel at a constant displacement rate while load and displacement data were recorded. A thermal camera recorded the heat emitted from each sample during the pull. The test allowed comparison of multiple samples for heat emission and hence ductility. In practice, several factors limit the method. First, the emissivity of the material will change if the material undergoes stress whitening due to crazing or cavitation. Second, the actual load on the sample is unknown, since samples mounted in parallel are never truly at the same strain, ie, one sample carries a greater percentage of the total load than others. Nevertheless, we found that the total energies emitted from a pair of polyethylene samples with known ductility differences reflected these differences, However, the heat emitted per unit strain from the samples is similar, the difference being the time to failure, which in a constant displacement rate test such as this is proportional to the conventional elongation to break. Therefore, the technique does add to the information obtained from the conventional test methods. A thermal image of two polypropylene samples during uniaxial testing is shown in **Figure 14**.

Figure 14. Thermal image in uniaxial tensile test of PP films of different ductility, similar heat output in later stages of deformation.
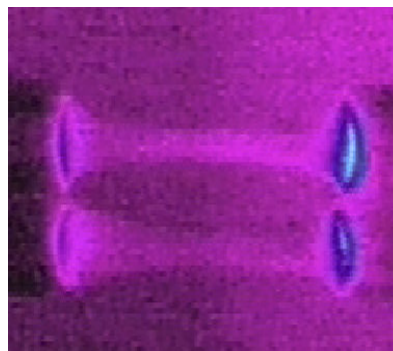
A biaxial test method was devised which allowed simultaneous testing of multiple samples of polymer film (ca 0.12 mm thick and 12 mm diameter) using pneumatic pressure. This device is shown in **Figure 15**. Pressure and displacement vs. time data were obtained

Figure 15. Thermographic biaxial pressure tester. Schematic of multi-well film pressure cell on left. Elements of the device are: (1) optical camera, (2) thermal camera, (3) Laser EDM, (4) Pressure cell.

Compressed Air
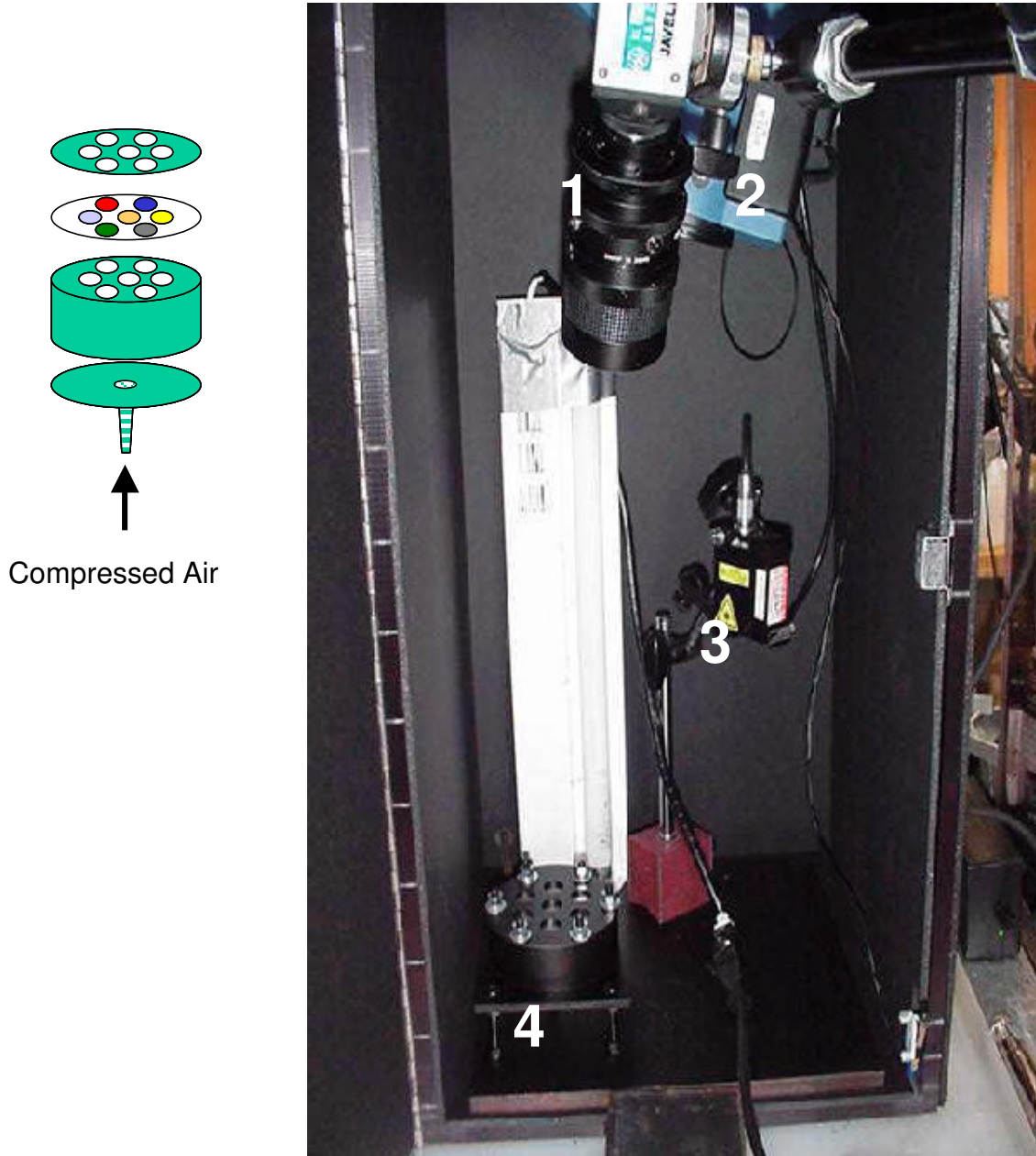
while a thermographic image was recorded. This method generated equal loading on all samples, provided that the samples' moduli and thicknesses were similar. Testing showed that

Figure 16. Thermal image of PEI in biaxial pressure testing. Scale at right shows relative temp. Range top to bottom is ca. 10C
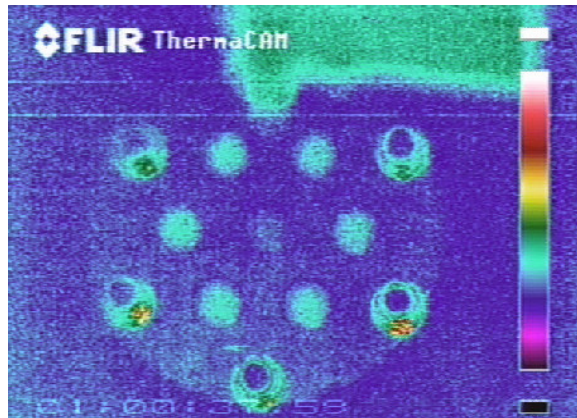
the thermal emission is similar during the plastic deformation stage from samples with very different ductility, but the displacement to break varies with conventional biaxial ductility, in a manner similar to the result obtained with the uniaxial tensile test described above. The conclusion drawn from our experimentation with this technique is that it does not yield additional information on polymer ductility from that obtainable more readily with method (2), miniaturized biaxial testing, and involves more extensive data analysis and interpretation. **Figure 16** shows a typical thermal image obtained with the biaxial apparatus, and **Figure 17** the corresponding normalized intensity plotted against time for two PEI materials of greatly differing biaxial impact energy.

Figure 17. Normalized thermal emission from PEI samples during biaxial pressure testing. Greater total area (energy) in more ductile material (a)
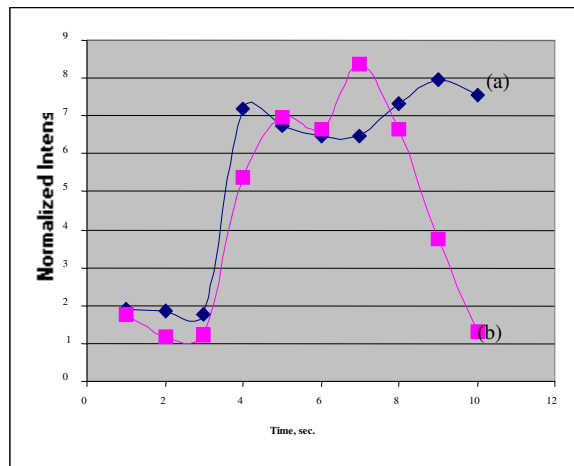
Micro-biaxial impact testing

This technique involved modifying the traditional biaxial impact test so that it could be applied to thin films or ribbons of polymer, and automated to allow rapid testing of the film at successive locations, thereby improving the statistics of the test. Previous work had shown the feasibility of sample scale down and miniaturized impact testing but had not demonstrated the possibilities of automation allowed by use of continuous film rather than discrete samples [51]. Scaled down versions of the conventional biaxial "Dynatup" impact tester were constructed which utilized constant displacement rate rather than a gravity driven dart and samples of extruded polymer films instead of typical 4" diameter, 1/8" thick molded disks. Two different instruments were prototyped: one based on an sewing machine in which the driver for a blunt

Figure 18. Prototype automated micro biaxial impact device.

10/50/100 lb
Load Cells

Conical/Hemispherical tup
0.5 mm radius

Film Roll From
Microcompounder

Air Clamps

Tape Drive Motor
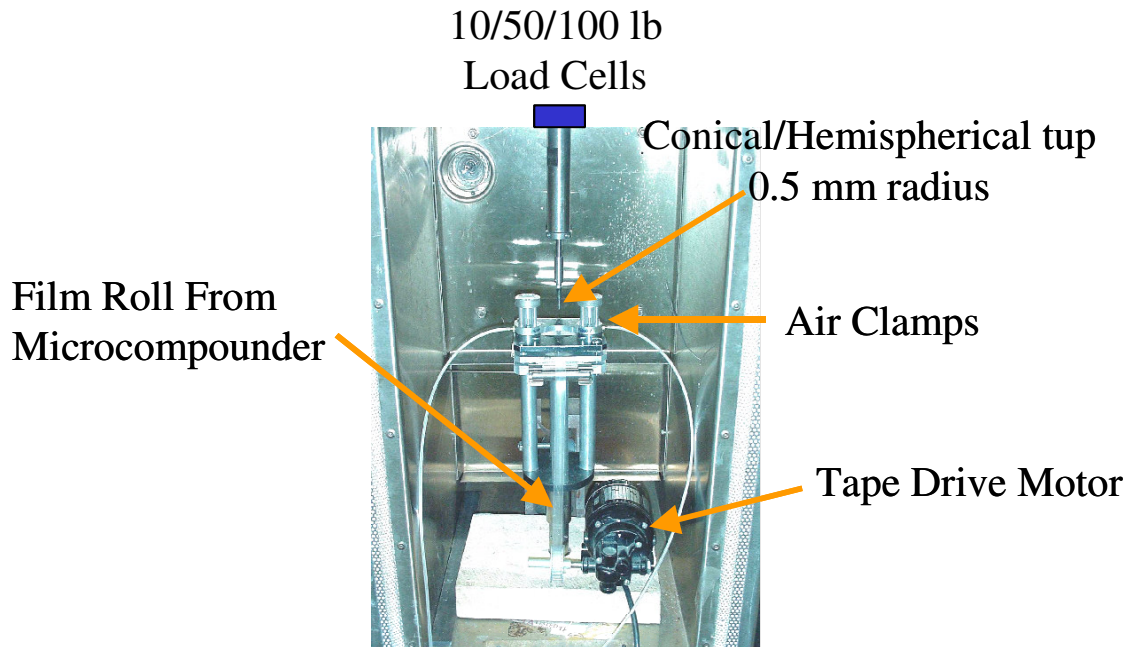
Max tup speed ca. 10 in /sec
Housed in environmental chamber (T/h control)

tipped needle was instrumented and the other based on a high-speed Instron hydraulic test system for driving a microdart. Both devices were constructed so that a continuous ribbon of film could be fed to the device. The implementation of this continuous feed is shown in **Figure 18** which shows the proto-type for the micro bixial impacter based on the Instron device.

Samples of polypropylene, polycarbonate, polyetherimide, and ABS pastic were evaluated in both conventional Dynatup fashion and with either of the systems based on the high speed Instron tester. In both cases, it was shown that load-displacement curves of each

impact event could be recorded which appeared to reflect the same type of behavior as seen for a conventional instrumented impact load-displacement curve and the relative changes in shape for increasing ductile materials paralleled the change in shape seen in the conventional tests. The difference between the impact behavior for the different materials can be seen in **Figure 19**

Figure 19. Ribbons of polymer following miniature biaxial impact testing, from top, PP, high rubber ABS, low rubber ABS.
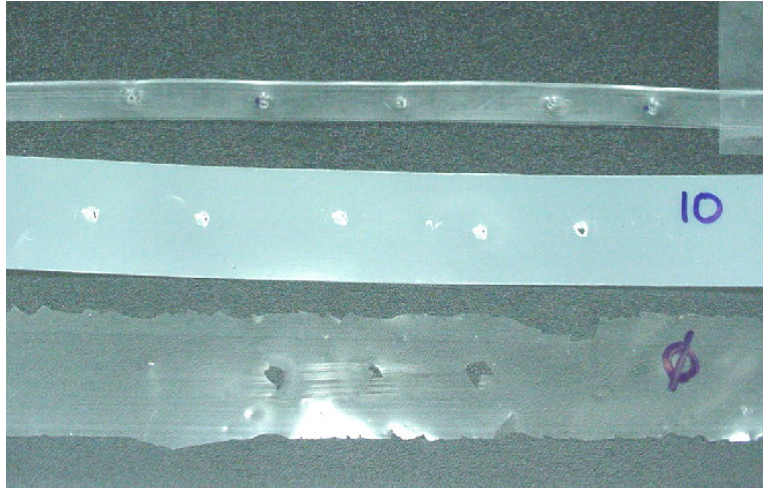
which shows a typical line of punches for microcompounder films of PP and high and low rubber (ductile and brittle) ABS materials. Subsequently, series of tests were devised using a set of ABS materials as well as polyetherimides and polycarbonates of progressively increasing ductility. Details of these validation tests are given in the Task 3 section.

Instrumented indentation:

Instrumented indentation is another set of techniques that was explored as a high throughput means for measuring mechanical properties [52]. Instrumented indentation is commonly called nanoindentation and differs from instrumented microindentation by the small loads (0.001N versus 1N) and diamond tips (Berkovich vs Vickers) that are used. Instrumented indentation involves the recording of a load-displacement curve as a diamond tipped shaft is inserted and then retracted from the surface of a sample (**Figure 20**). This data can then be

Figure 20. Schematic of instrumented indenter (Left). Load displacement curve from indentation (Right).
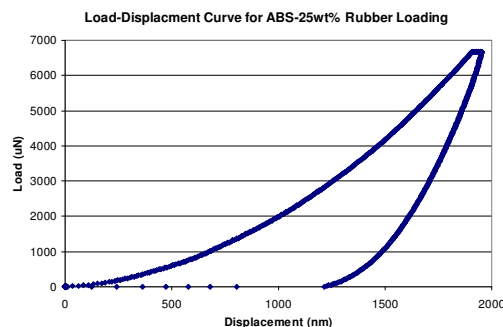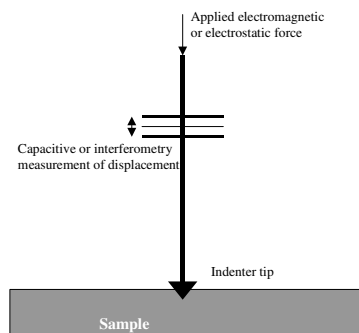
analyzed to obtain the elastic modulus, hardness, and work of indentation. [52] In addition, dynamic mechanical properties (E', E'', and tan δ) can be measured by oscillating the tip [53]. The sizes of the indentations vary from 10-10,000nm in depth for nanoindentation to tens of microns for microindentation.

 The small size of the indentations means that less material is required for testing which allows for high throughput screening or measurement of mechanical properties either on a series of small samples or across a gradient library. The objective of these indentation experiments was to investigate the correlation between the mechanical properties measured by instrumented indentation and those measured by more common macroscale mechanical measurements. In our experiments, the intended correlations were indentation elastic modulus with uniaxial tensile modulus, hardness with tensile yield strength, and the plastic work of indentation (plasticity index) with ductility.

 Both microindentation and nanoindentation were performed on the ABS test samples (0, 15%, and 25% rubber loading) that were used in the validation studies for biaxial impact testing. In each case, the samples were as-molded Izod bars of the ABS. Sample surfaces were only prepared by a light cleaning of methanol prior to testing to remove any dirt or fingerprints. The microindentations were performed on a Zwick commercial microindenter. A full gauge repeatability and reproducibility matrix was performed involving measurement of the hardness, elastic modulus, and plasticity index (plastic work of indentation) by taking 5 points on each specimen with two replicate sets of measurements and two operators. Nanoindentation experiments were performed on a Hysitron Triboindenter™ machine using the same three compositions with one operator.

Table 5. Indentation gage performance.

	Hardness (MPa)	Elastic Modulus (GPa)	Plastic Work
Gauge Precision-microindentation	1.4	0.067	0.0044
Operator Significance	No.	Yes.	Yes.
# of levels distinguished-microindentation	77	20	7
Gauge Precision-nanoindentation	14.7	0.12	0.018
# of levels distinguished-nanoindentation	11	14	5

 The experimental precision of both indentation techniques was sufficient for discriminating between the ABS standard samples for all three property measurements (**Table 5**). The operator contribution to experimental error for microindentation was negligible for hardness and barely significant for modulus and plastic work. For both techniques, plastic work was a mediocre gauge for discriminating samples across the ABS series. The reason for the higher precision of microindentation is most likely due to the substantially greater depth of the indents compared to the small depths of the nanoindentations.

 Both microindentation and nanoindentation showed linear relationships between the rubber loading and the mechanical properties measurement (**Figure 21**). In each case, reductions in the elastic modulus and hardness were observed with increasing rubber content, as was expected. The elastic modulus values between the two indentation techniques differed by less than 10 percent for all three compositions; while the differences in hardness between

Figure 21. Hardness and elastic modulus as a function of rubber content for nanoindentation (Right) and microindentation (Left).
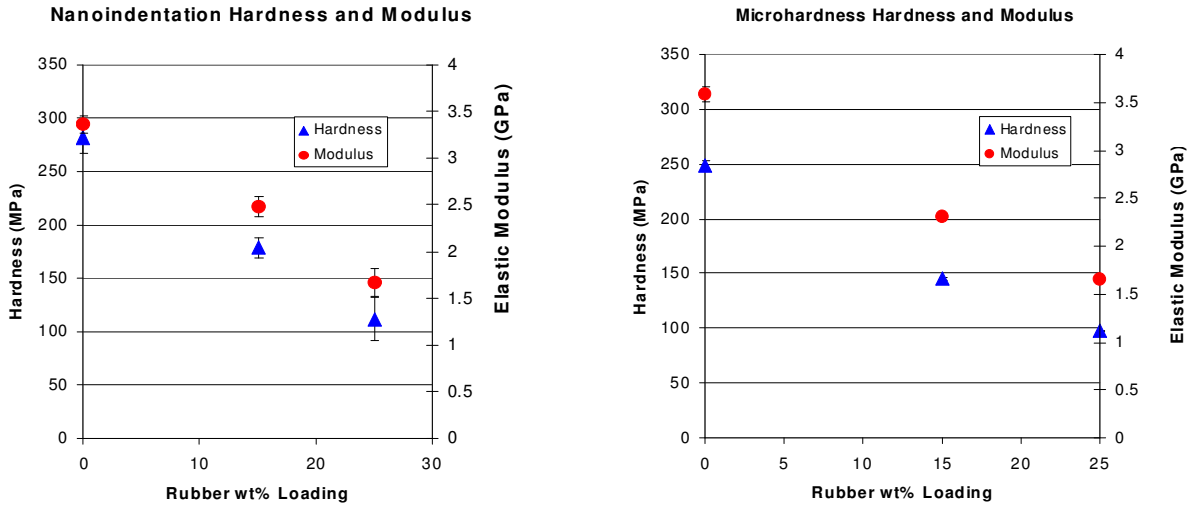
the two were 13-20 percent for a given composition. The plastic work of indentation increased slightly with increasing rubber content, but with a much weaker sensitivity than the other properties. The correlation between elastic modulus measurements from microindentation and macroscale uniaxial tension experiments was fairly strong (**Figure 22**), but microindentation consistently underestimated the elastic modulus observed by the macroscale testing.

Figure 22. Correlation between microindentation modulus and macroscale modulus measurements.
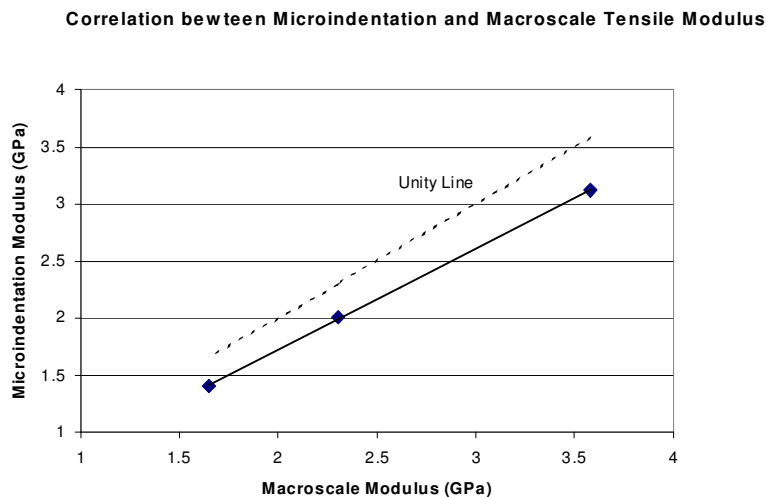
Using the Tabor relationship (eq. 2) [54], which connects hardness with flow stress at 8% strain, we compared estimates of the yield strength from the hardness measurements with

the measured value of yield strength from the macroscale, uniaxial tension experiments, where σ is the yield strength, ε is the strain, and H is the hardness (**Figure 23**).

Figure 23. Estimates of yield strength from hardness measurements compared with macroscale measurements of yield strength in uniaxial tension.
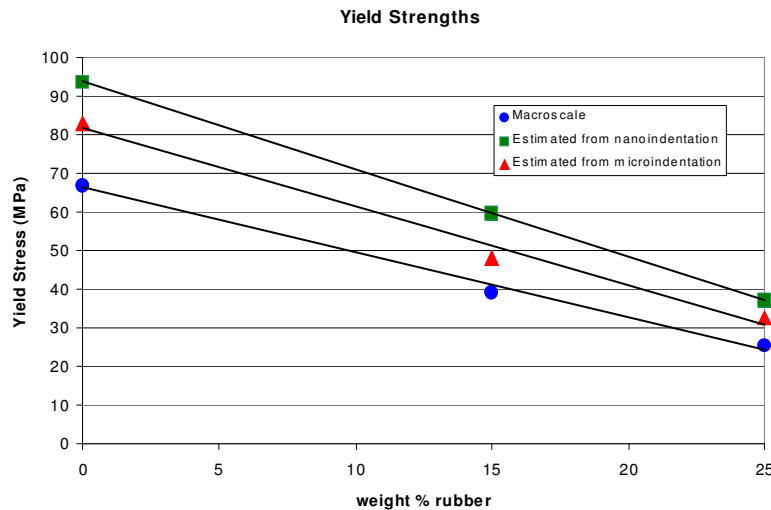
$$\sigma(\varepsilon = 0.08) \approx \frac{H}{3} \qquad \qquad (2)$$

The estimated and measured yield strengths all had approximately the same slope. However, both indentation techniques systematically overestimated the hardness. This overestimation could stem from a faulty assumption of equality between the flow stress and the yield stress, skin effects on the as-extruded part, or from something more fundamentally different about the indentation test compared with uniaxial tension.

In summary, the correlation between instrumented indentation techniques and macroscale measurements of mechanical properties in ABS polymer standards had mixed success. Indentation elastic modulus could certainly be used to rank order materials, if not measure an accurate value of the modulus. Hardness did correlate with yield strength and may be used to rank order polymer strength, but cannot provide a direct, accurate measurement of yield strength. The plasticity index was only a weak function of the rubber loading and may not be able to adequately discriminate amongst polymers with differing impact toughness values. Since indentation instruments are commercially available, no additonal validation work was performed on these devices. However, any effort to implement these devices for measuring properties of polymers will require additonal effort to prepare samples which incorporate the appropriate size, configuration and compositional variations for combinatorial studies.

Ultrasonic analysis

Ultrasonic probes have been shown to have numerous applications in the field of polymer characterization. Ultrasonic methods utilize piezoelectric transducers for the generation and detection of mechanical waves. When propagated in polymeric materials, these waves are influenced by the polymer's structure, as well as by molecular relaxation processes. Velocity and attenuation measurements can be used to estimate the viscoelastic properties of polymer melts [55], and have been used to monitor polymer processing [56]. Several studies have demonstrated the power of ultrasonic evaluation of polymers, including: (a) flow behavior of molten polymers [57]; (b) viscosity and thermal degradation [58]; (c) composition and morphology of mixtures and blends [59]; (d) concentration, size, and dispersion of fillers [60]; (e) residence time distribution in extruders [61]; and (f) orientation measurements [62]. It was determined that a high temperature (900 °F) transducer was necessary for operation at the microcompounder die. A supplier was located that indicated that they could build a die of the appropriate specifications. However, upon receipt of the transducer it was determined to be of poor quality and incapable of achieving even the minimum specifications. After a number of additional efforts to obtain an appropriate transducer, the effort in the area was suspended in favor of concentrating on the other test methods.

Task 3—Generate system development strategy.

Task 3.1—Perform statistical analyses of individual microanalytical techniques and apply results to further refine Task 2 development.

Statistical analysis of traditional MFI measurement

Many of the microanalytical tests developed in this project are directed toward a prediction of the melt flow index of polymers or a prediction of the same rank ordering of stabilization (degradation) that would be obtained from a comparison of MFI results. In order to conduct these comparisons, it is important to know the typical variability obtained when conducting these tests. To this end, a single operator gage study was performed using three PP samples which had nominal MFI values of ca 7, 15, and 21 g/10 min. The MFI's were obtained according to the ASTM D1238-95 standard using a Dynisco Kayeness Polymer Test System, Series 4000, Model D4004. The sample conditions were 230 °C and 2.16 kg weight with 420±30 s melt time. Five different samples of each material were tested with two measurements obtained for each sample (for a total of 10 measurements per material). The total standard deviation across the ten measurements for each material amounted to less than 3% of the mean. This study indicated that 99% of the overall gage variability is captured in a 2 MFI unit range.

Statistical analysis of spectroscopic method for MFI determinations

The variability of the method for spectroscopic determinations of MFI was evaluated using materials produced in conventional and micro-extruders. For these evaluations, we used multiple replicate individual samples of polymers with different MFI and analyzed their spectroscopic responses. The goal of the analysis was to determine the factors affecting the

quality of the collected data. These factors included extrusion temperature, type of additives, and others.

      Figure 24 illustrates spectra from replicate samples with two different MFI values. The

Figure 24. . Spectroscopic analysis of solid replicate polymer samples with different MFI values produced in the microextruder: (A) MFI=4.5 and (B) MFI=19.5.
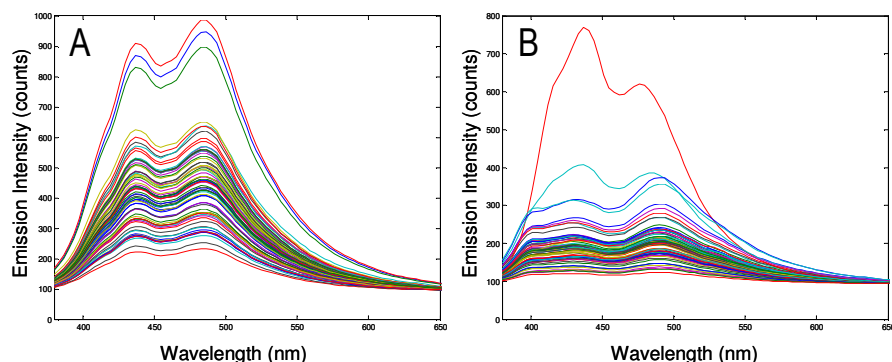
significant variation in signal intensity is caused by the different geometry of the solid samples and thus, different amount of light collected by the instrument. Thus, we used a ratiometric approach where a ratio of peaks in the spectrum was used for quantitation. The results of the ratiometric determinations are presented in **Figure 25**. Clearly, this approach provides a

Figure 25. Statistical analysis of ratiometric approach for determination of MFI using spectroscopic tools. (A) Signals from two polymer materials with the minimum and maximum MFI vales. (B) and (C) Histograms of ratiometric measurement capabilities of low-and high MFI materials, respectively. Solid line – short-term capability, dotted line – long-term capability. For fit values see Table 6.
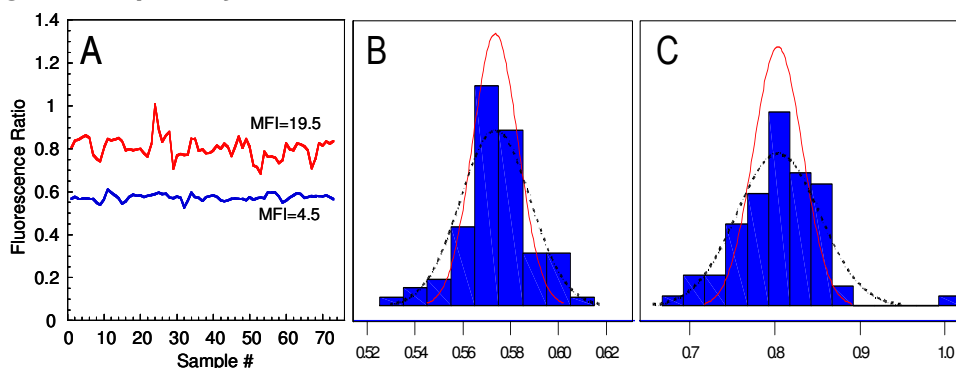
significant improvement in the precision of determinations compared to intensity measurements. Results of the statistical analysis using Minitab software are presented in **Figure 24 B** and **C** and summarized in **Table 6**. A close comparison of the variation of determinations of materials with low and high MFI values indicates that the variability of determinations of high MFI values is

more than 10 times higher compared to low MFI values. Contributions to the variation have been identified as both process and instrumental sources and the strategies for their reduction have been outlined.

Table 6. Results of the statistical analysis of variability of ratiometric spectroscopic determinations of MFI.

Standard deviation	MFI (g / 10 min)	
	4.5	**19.5**
Short-term	0.009	0.28
Long-term	0.014	0.48

Statistical analysis of torque changes during extrusion for MFI determinations

The torque measurements outputs from the microcompounder were collected using a data acquisition board and LabView software supplied by National Instruments, Inc. Typically, these values were collected along with the feeder delivery outputs (see Task 4) once every four seconds. Each condition was run for at least 10 minutes with the last two minutes collected as a steady-state operation. We found that typically, within each condition (feedrate, extruder rpm and temperature), the steady state torque variation was less than 2% of the mean torque. However, two issues were noted involving the reliability of the torque measurements in the extruder. One was that the starting state of the extruder screw and barrel had a significant effect on the absolute value of the torque recorded (even though within a run the torque might have low variability). Any residual material residing in the barrel or on the screw can change the torque reading. Second, any unusual upset during the run (intermittent shut-down, feeder malfunction leading to high rate or loss of feed, etc) shifted the absolute value of the torque and resulted in a relatively long re-stabilization period. For this reason, it was determined to look at the differences in torque for each stabilized PP material relative to unstabilized PP controls. In this manner, significant shifts in the absolute values of torque due to process shifts could be managed.

A series of tests were run to estimate the variability in the measured torque differences versus the MFI's for a set of materials. In these tests, six PP compositions (A-F) containing 1000 ppm each of different stabilizers were prepared and run on different days under the abusive conditions outlined in Task 4. On each day, each composition was run twice and the order in which the twelve stabilized compositions were run was fully randomized. Before and after each of the stabilized compositions were compounded, an unstabilized PP control was run. The automated feed system was set for a total run time of 10 minutes for each material. Pellet samples were collected for MFI measurements during the last two minutes for each material The torque values were collected every 4 s throughout the run but only the last five minutes were used for the torque averages. The delta torque values were calculated by subtracting the averages of the torque for the unstabilized PP materials that were run before and after each stabilized material from the average torque for the corresponding stabilized material. The MFI and delta torque results for all 24 materials are shown in **Figure 26** along with a designation of their corresponding compositions (A-F). The replicate samples are clustered reasonably well – the most stabilized materials (highest delta torque, lowest MFI) are clearly distinguishable from the less stabilized materials (lowest delta torque, highest MFI). Distinguishing degrees of moderate stabilization with either MFI or delta torque measurements would appear to be

Figure 26. Relationship of delta torque vs MFI for replicate samples of six stabilized PP compositions.
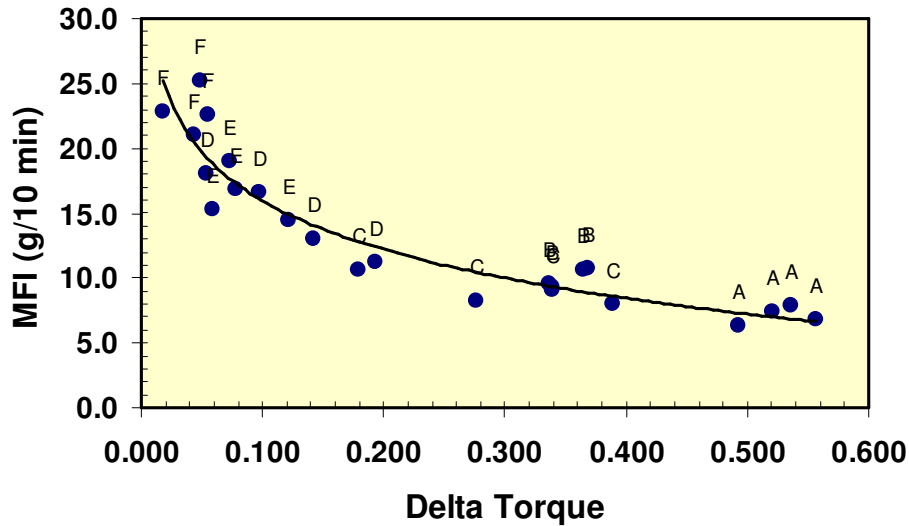
difficult. Also, one composition, C appears to have more variability in delta torque that all the others. **Figure 27** illustrates the degree of variability within each test across the replicates within each composition where the means for each composition are plotted with the error bars corresponding to +/- one standard deviation.

Figure 27. Average delta torque vs average MFI for replicate samples of six stabilized PP compositions. Error bars correspond to one standard deviation for the measurements within the replicates.
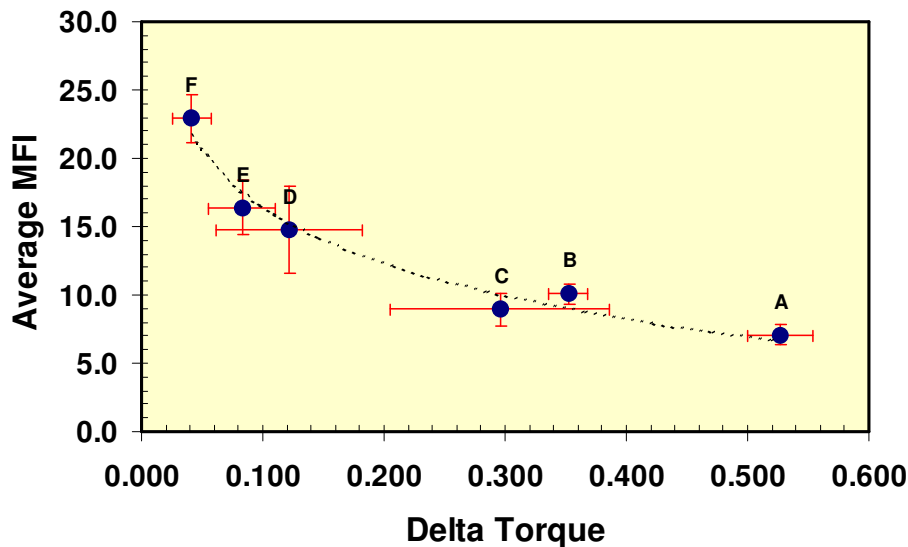
Statistical analysis of extruded pellet melt behavior for MFI determinations

As stated in Task 2, we had noticed that pellets of PP that had been extruded in the microcompounder melted in a manner that appeared to depend on their MFI after extrusion. In order to test this relationship, we initially used simple measurements of the initial length of each pellet (nominally 4-5 mm) and the length of the pellet after a rapid exposure to 300 C (on a glass slide placed on a heated stage) for a brief period of time. These differences in pellet length after melting were then compared to the MFI measured for these materials. The influence of time alloted for the pellets to melt and the addition of a PTFE release spray on the slide were investigated. No strong influences of these factors were seen with the exception that longer time (60 s) exposure increased the variability. One of the issues in using this method is that it relies on the measurement of small samples and a relatively small change (<0.5 mm). As might be expected under these conditions, relatively high variability is obtained. In order to minimize the effect of uneven pellet cuts, the ends of the pellets were trimmed with a razor before the initial measurements. Most experiments were run with 3 pellets of each material and the averages of those **d**(elta)**L** measurements were used. The relative standard deviation of the dL measurements was estimated to be about 20%. Despite this large variability, as will be shown later in this report, the averaged replicate dL measurements appear to be viable as a <u>screening tool</u> to highlight high performance PP stabilizers from those that are poor to ineffective. Attempts were also made to automate the pellet dimension measurements using an imaging system, but they did not prove successful. However, it still appears possible to use an automated imaging system if a greater amount of the 2D/3D shape information contained in the image could be incorporated rather than the simpled dimensional changes that were used in our original studies.

Statistical analysis of chemiluminescence imaging of thermooxidative stability of materials arrays

The variability of the CL imaging method for determinations of thermooxidative stability of polymer arrays was evaluated using materials produced in conventional and micro-extruders. For these evaluations, we used multiple replicate individual samples of polymers with different MFI and analyzed their CL responses. The goal of the analysis was to determine the factors affecting the quality of the collected data. These factors included the nonuniformity of the isothermal heater to keep an array of materials at a selected operating temeperature, the nominal operating temperature, the distance between samples in the array, composition of atmosphere to which the array is exposed during testing, and others.

Representative kinetic CL profiles from replicate samples are depicted in **Figure 28**. This data illustrates an excellent reproducibility of the kinetic profiles for the selected test conditions. The figure of merit for the response is selected as the time to reach the maximum signal. Under our test conditions, the variability of this parameter Dt was less than 4 min (see **Figure 28**). Taking into the account the actual average time to reach the maximum signal was 66 min and the standard deviation of Dt measurements of 1.6 min, the precision of determinations was calculated to be better that 3% relative standard deviation.

Figure 28. Representative kinetic CL profiles for replicate polymer samples from a typical imaging experiment. The figure of merit for the response is the time to reach the maximum signal. The variability of this parameter is Dt.
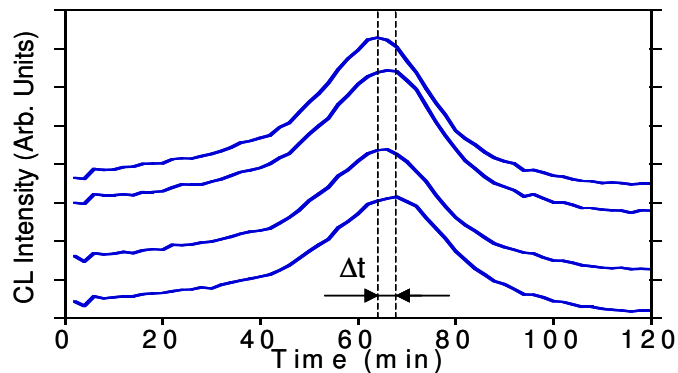
Statistical analysis of performance of 24-channel acoustic-wave transducer array

From a previous project, we have identified that noise reduction is important in optimizing the resolution of the transducer system [63]. Typically, noise magnitude of analytical instruments is reported in root-mean-square (RMS) values [64]. In acoustic wave devices, thermal, amplifier, filter, detector, and oscillator noise sources contribute to total noise [65]. Similar to our previous work based on a sensor array with a smaller number of crystals [31], we determined that the main parameter that affected the noise in frequency measurements in our system was the sampling interval. The sampling interval T included n frequency measurements with a 10-ms gate time each, T (ms) = 10n (ms). Typical noise levels in the sensor system at different sampling intervals are presented in **Figure 29**. At small sampling intervals, the RMS

Figure 29. Minimization of noise level in the developed transducer system by selection of the optimal sampling interval.
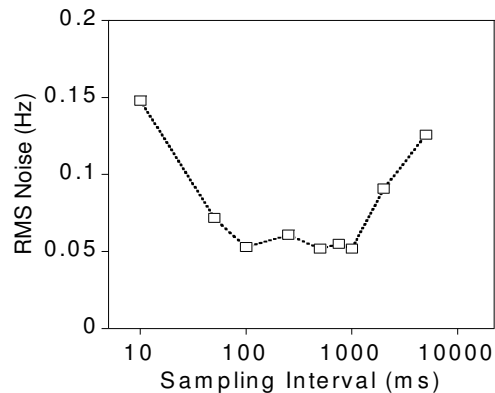
noise was about 0.15 Hz but it rapidly decreased down to about 0.05 Hz with an increase of T to 100 – 1000 ms. These sampling intervals provided the minimal noise. Further increase of T resulted in an increase in the RMS noise, due to the redistribution of the weighting factors of each of the noise sources at longer T. This analysis optimized our 24-channel sensor system for further evaluation of a viscoelastic, vapor-sorption, and other properties of polymeric materials.

Statistical analysis of static dissipation measurements

We investigated several variables that affect the static decay measurement, including the relative position of the charging electrode and the measurement probe, charge polarity, magnitude of the initial charge, and the methods of extracting a meaningful performance rating from the observed data. Of particular interest was the time required to make a single measurement, to ensure that the method can be used to evaluate and rank a fairly large number of samples within a timeframe compatible with the combinatorial production approach, and the other evaluation tests being conducted on those same samples.

Figure 30 shows replicates of voltage versus time curves for a polycarbonate specimen containing an anti-stat additive at a concentration of 1.8%. The corona charger was placed 1 cm above the sample, and the voltmeter probe positioned about 2 mm from the opposite face of the sample (see **Figure 31a**). At time = 0, there is no charge on the sample surface. When the

Figure 30. Replicate static decay curves for a single sample of polycarbonate containing 1.8% anti-stat additive (geometry of measurement shown in Fig 31a).
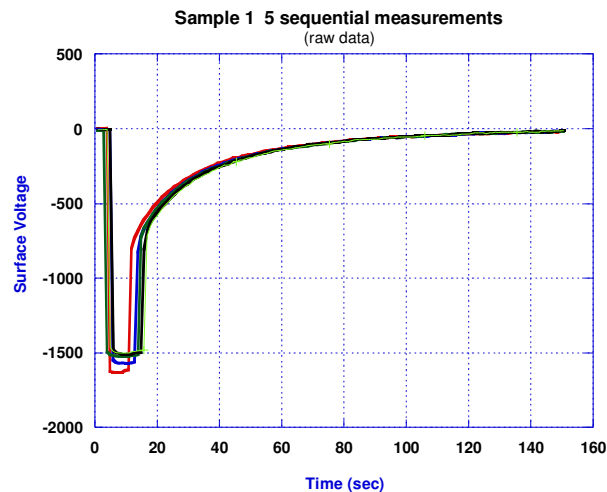
corona electrode is energized (-10 kV), the surface of the plastic reaches a steady-state charge V0 that depends on both the sample characteristics and the experimental conditions. When the voltage is manually switched off, the surface voltage decays to zero in about 100 seconds, consistent with previously reported measurements for similar formulations. The value V0 and the overall static decay curves are reproducible; the curves agree even more closely if one corrects for the different time offset between the end of the charging cycle and the beginning of the voltage decay measurement.

In comparing the experimental geometries A and B (**Figure 31**), it was found that the magnitude of V0 was lower in A, especially for samples with poor static dissipation. Since static

Figure 31. Schematic of experimental geometries for corona charging. A = Stationary sample, B = Sample moved between charger and ESVM probe.
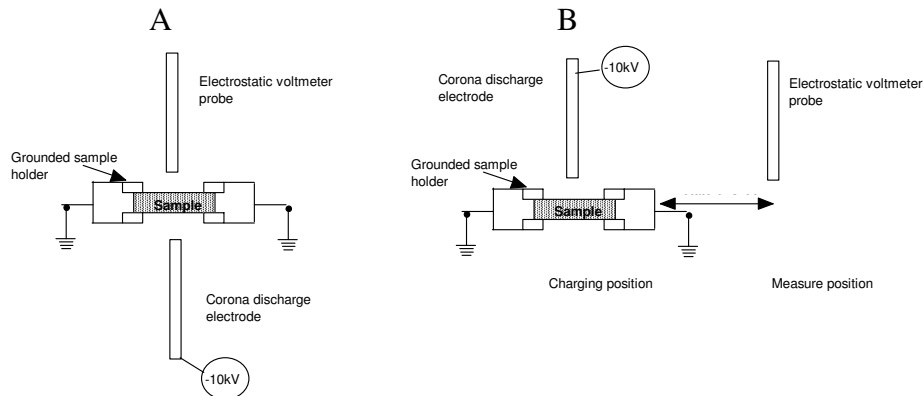
charge is a surface phenomenon, it is likely that geometry B is more effective at delivering the charge to the surface in closest proximity. Charge transport through the material to the opposing surface is unlikely for the materials due to their very high bulk resistivity, but some sort of induced charge may be present on both surfaces. It is also possible that in geometry A, the voltmeter probe is detecting the voltage on the opposite side, or a combination of the charges on both surfaces. For the remainder of the measurements described in this report, the charging electrode and the measurement probe were positioned on the same side of the sample. This introduces the complication that the sample must be moved from the charging position to the measurement position, and introduces additional variability into the overall measurement. For example, part of the initial surface charge may have already dissipated during the time the sample is being moved into the measurement position.

Figure 32 shows replicate measurements of the static decay curves for a single sample of polycarbonate containing 1.8% anti-static additive, using geometry B (**Figure 31**), where the

Figure 32. Replicate static decay curves for a polycarbonate ribbon rotated between the charging electrode and the measurement position.
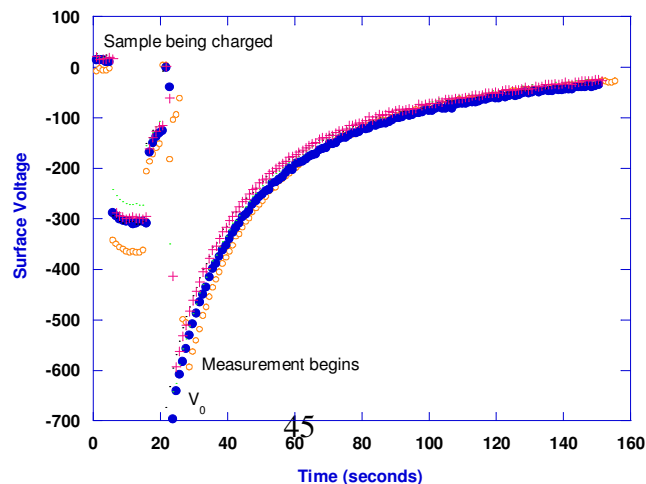
sample is moved between the charging electrode and the measurement position. Note that there is considerably more variability in the absolute magnitude of the initial charge. The variability is significantly improved by processing the data by applying two corrections. From the raw data (time versus voltage), the time data is adjusted to set t=0 at the point where the voltage is at its largest absolute value (defined as V0). Next, the voltage at each time is normalized to V0. The resultant V/V0 versus time plots for all samples then show a decay curve starting at V/V0 = 1.0 and extending to lower values, roughly exponentially approaching zero. The data of **Figure 32** are re-plotted after applying these corrections in **Figure 33**.

Figure 33. Data of Figure 32 after applying data reduction scheme described in the text.
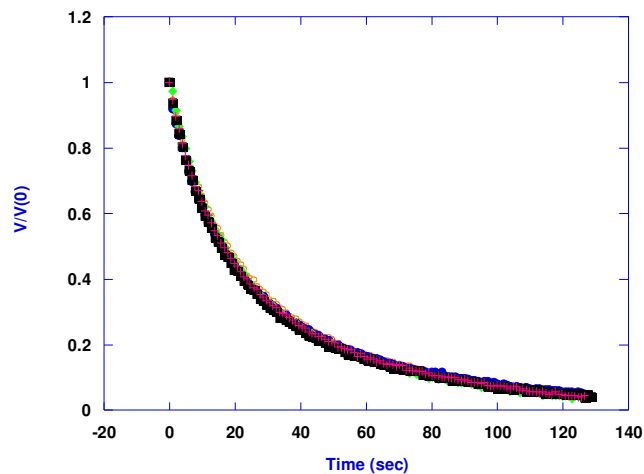
Based on equation (1) (Task 2.2, page 28), one would expect that a plot of ln{ V/V0} versus time would provide a straight line with a slope of RC, characteristic of the material's electrical properties. However, this reduction scheme did not produce a good fit to any of the data sets that were obtained in our studies. Empirically, it was found that most of the static decay curves could be characterized by a two-exponential fit of the form:

$$V/V0 = m1*exp \{-t/ m2\} + m3* \{-t/ m4\} \qquad\qquad \textbf{(3)}$$

Figure 34 shows typical static decay data processed by the scheme described above and curve fit using equation (3). Although the physical significance of the parameters is not understood, it is reasonable that the static decay performance of materials can be evaluated (or specified) by the magnitude of the curve fit coefficients. In general, the magnitude of both m2 and m4 decrease with increasing static dissipation rate, whereas we found no correlation to the scaling coefficients m1 and m3.

The static decay performance is often evaluated by measuring the time required for an induced charge V0 to decay by some fraction of its initial value, for example 50% or 90%. This may require collecting voltage data at closely spaced time intervals. However, if the data can be collected at larger time intervals, then curve fit using an appropriate function, the 50% or 90% decay times can be found by interpolation.

Figure 34. Typical curve-fit results for static decay curve using equation (3)
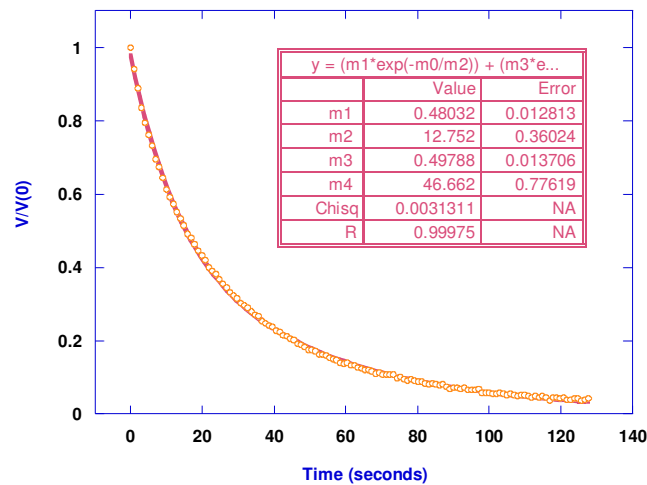
Based on our findings, we envision that an experimental arrangement with multiple samples, along with a data reduction scheme as described above, is feasible for measuring the static decay curves for a number of samples simultaneously. Multiple samples can be sequentially moved to position each under the corona charger. After the charging cycle, the samples are then sequentially moved to the measurement position in a repetitive cycle to record the time versus voltage curves. Note that the absolute time values for each individual sample's data will be offset, which can be described as "interleaved time sampling". The static decay performance is then evaluated by the value of the curve fit parameters, or an interpolated time value corresponding to a specified degree of voltage dissipation.

A working protoype of such a device has been made and an additional alternative design has been documented. Additional business sensitive details are described in internal GE communications.

Statistical analysis of micro-biaxial impact measurements

One complication for the micro-test relates to significant variability of the thickness of the films tested. The impact energies vary with sample thickness. The test films produced had significant variability in thickness. Conventional testing typically uses injection molded plaques of 0.125" thickness and the variations in thickness are small relative to the average sample thickness. In order to compensate for this issue, all analyses dealt with normalized impact energy values where the energy was divided by the sample thickness.

For both highly ductile materials, such as polycarbonate and moderately ductile materials, such as polyetherimide, the standard deviation of the micro-biaxial impact energy normalized by sample thickness ranged from 5 to 20% of the average energies. These values are similar to those obtained in conventional instrumented dart testing. In conventional testing, lower variabilities in the energy values are obtained for more ductilie materials and higher variabilities for lower ductility samples. The advantage of being able to test many more samples in an automated micro-biaxial test should ultimately lead to better estimates of the average values.

   Task 3.2—Validate microanalytical techniques

   Spectroscopic method for MFI determinations
      In a series of validation experiments, in-line determinations of MFI were performed on both conventional and microextruders. Initially, a conventional extruder was used for feasibility demonstrations of the developed measurement approach. The different amounts of degradation were induced by having polymer compositions with different stabilizers and by exposing the polymer to variable amounts of air during the extrusion by opening one or two air vents. The reference MFI values were obtained by chopping the extruded polymer strand and

Figure 35. Response of an in-line spectroscopic probe to the variation in the MFI of polymeric compositions during the extrusion process. (A) Total and (B) low-MFI ranges of performed experiment. Reference MFI values are shown in boxes for each condition. Polymer stabilizer (concentration, ppm): a = unstabilized; b = U668 (1000); c = U210/668 (1000/1000); d = U210 (2000); x = restart; y = one port unplugged.
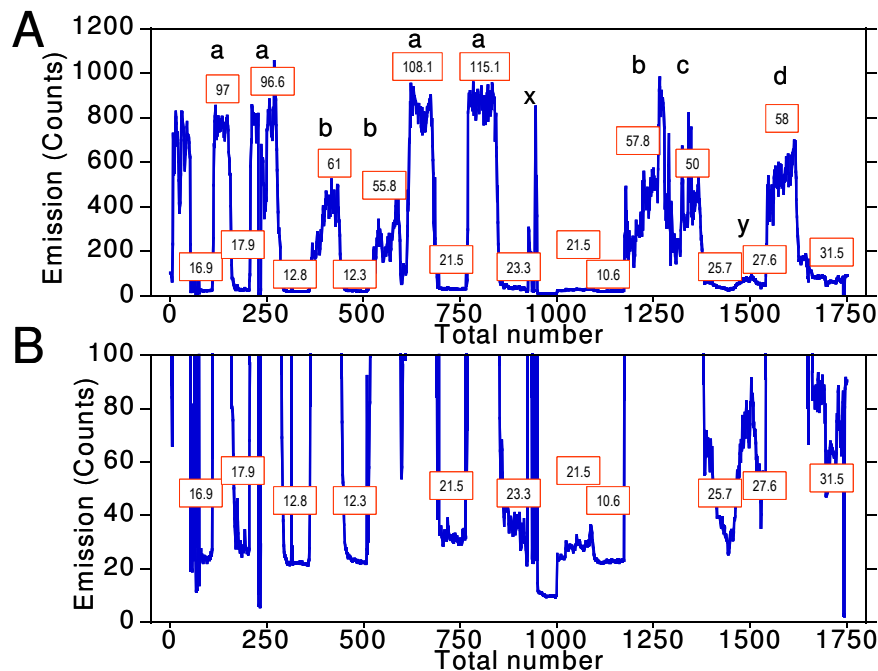
collecting the pellets for off-line analysis.

Response of the in-line spectroscopic probe to the variation in the MFI of polymeric compositions during the extrusion process in the conventional extruder is illustrated in **Figure 35**. This figure demonstrates the dramatic signal changes from extruded polymer which are correlated with the amount of air during the extrusion. Clearly, these signal changes are significantly modulated by air-induced polymer degradation. Further, correlation between the stabilization efficiency of different anti-oxidants and the detected signal is also observed. This was indicated by the signal differences between these different polymer compositions in both air-rich and air-depleted conditions. Under air-rich conditions, the signal differences between different materials were more pronounced compared to the signal differences in air-depleted atmosphere.

A correlation between the MFI and in-line spectroscopic signal is presented in **Figure 36**. This data demonstrates that the highest sensitivity in MFI determinations is provided over the MFI range from 20 to 60 g/10min with a slight decrease in sensitivity over the the initial MFI values of less than 20 g/10min.

Figure 36. Correlation between the response of the in-line spectroscopic probe and MFI of polymeric compositions during the extrusion process detailed in Figure 35.
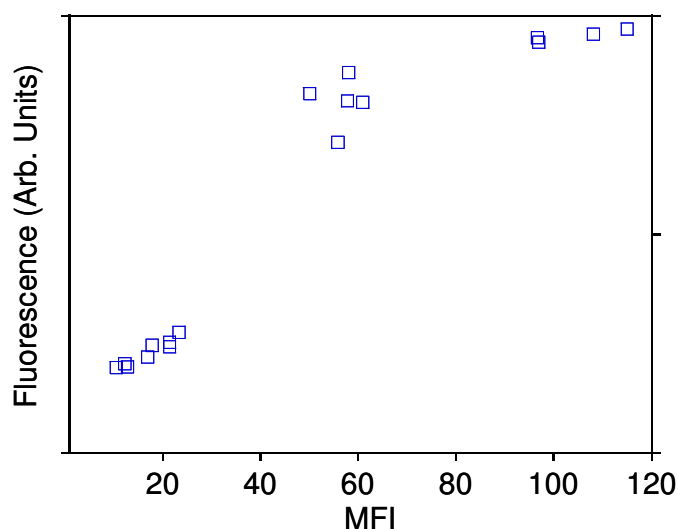
Similar experiments were performed on the microcompounder. The variation in the thermal oxidation was induced by changing the extruder atrmosphere from air to argon. Experiments were performed at two temperatures, 230° and 260° C in order to determine the temperature-induced contributions to the spectroscopic signal and the signal change upon variable atmosphere composition. Results of in-line determination of thermal oxidative stability of polymers during microextruding experiments are presented in **Figure 37**. These plots demonstrate that under the microextrusion conditions, thermal oxidation of polymer strongly depends on the amount of oxygen in the extruder. The temperature dependence is also slightly pronounced in the larger initial signal from the degradaded polymer and overall larger signal change from air to argon atmospheres.

Following this work, the fluorescence spectra of a number of process and UV stabilizers in PP were investigated The use of multivariate fluorescence spectral analysis with a limited

Figure 37. Results of in-line determination of thermal oxidative stability of polymers during microcompounding experiments. Temperature conditions, °C: (A) 230 and (B) 260. Changes from air to argon and back are shown with arrows. Slight offsets are due to the delay in extruder response.
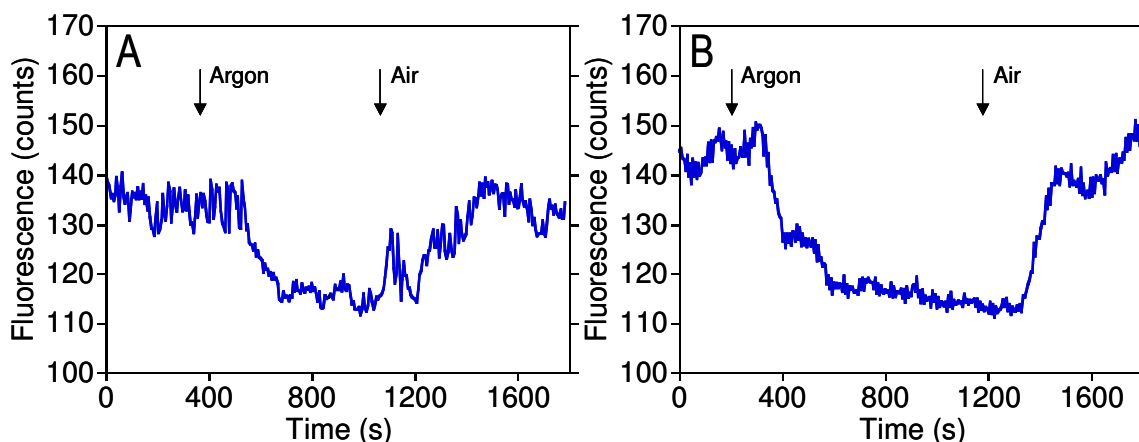
number of excitation wavelengths showed some promising results for a subgroup of the polymer compositions. There were several factors that induced some complications. One fo the factors was photodegradaton of polymer compositions under an excitation UV light that caused a change in fluorescence spectra during data acquisition. Another factor was the periodic excitation of polymer impurities and/or polymer additives that caused spectral changes as well. Collection of both excitation and emission spectra could be used for removal of such spectral interferences [66], however, such an automatic system was unavailable and could not be tested. Even without such a system, this work does indicate that for a smaller set of stabilizers with a particular polymer where these interferences can be more easily managed, this approach can be useful in a high throughput system for optimization of stabilizer performance.

Validation of Multivariate Methods for Simultaneous Analysis of Color and MFI

Experimental validation of the method for simultaneous analysis of color and MFI was performed using a set of diverse polypropylene samples with YI ranging from 2.4 to 10.3 and MFI ranging from 4 to 30. The samples were prepared from six formulations and multiple pass extrusions performed at 260 °C in air. Pellets of each formulation were positioned in a 48-array block to provide two measurement replicates of each formulation. Fluorescence measurements of samples arranged in the array format were performed on a modular spectroscopic setup built in house.

The spectral data was collected from solid samples and arranged as an emission wavelength – fluorescence intensity response matrix. Analysis of data was performed using a multivariate analysis toolbox such as PLS_Toolbox software package (Eigenvector Research, Inc., Manson, WA) operated with Matlab software (Mathworks Inc., Natick, MA). A multivariate

calibration method, Partial Least-Squares (PLS) regression was used to quantify the variations in spectral features as a function of YI and MFI.

The predictive performance of the developed PLS model was assessed using the leave-one-out cross-validation (CV) method [33]. The root mean squared error of cross-validation (RMSECV) was the estimator of the quality of the PLS model. Results of the multivariate PLS analysis of the normalized fluorescence spectra of polypropylene pellets to predict YI and MFI values from the spectral features are presented in **Figure 38**. **Table 7** summarizes the results of the PLS modeling for prediction of YI and MFI. This data demonstrated the applicability of the method for analysis of MFI and YI across diverse types of polymer compositions.

Figure 38. PLS calibration results of polypropylene pellets to predict (A) YI and (B) MFI.
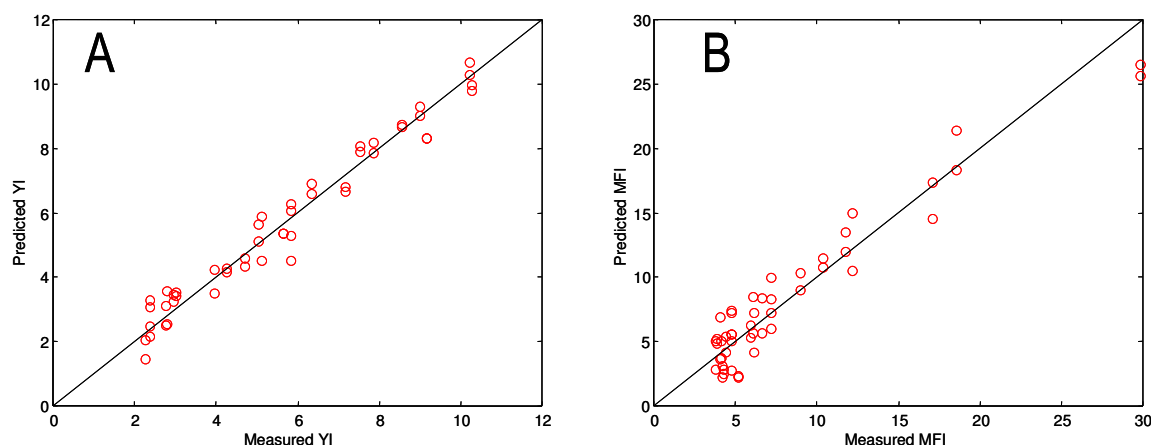
Table 7. Results of the PLS modeling for prediction of YI and MFI.

Number of latent variables	Calibration error	Cross validation error
YI		
5	0.76	0.91
3	1.16	1.28
MFI		
5	2.2	2.98
3	3.4	3.76

Torque changes during extrusion for MFI determinations

The trend shown in **Figure 26** between the delta torque in the microcompounder and the MFI measured for the corresponding extruded PP composition demonstrated the strength of the predictive relationship of torque to MFI. It indicated that the delta torque could be determined during the process run, used to estimate the MFI and no additional testing would be needed to differentiate the stabilization effectiveness of various additives. In addition to the 24 data points

(6 compositions, repeated 4 times) shown in **Figure 26**, an additional series was run with 11 compositions comprised of various combinations of additives. The relationship of the delta torque to MFI for all 35 materials in shown in **Figure 39**. The data has a reasonable fit to a logarithmic relationship.

Figure 39. MFI vs delta Torque for various PP compositions
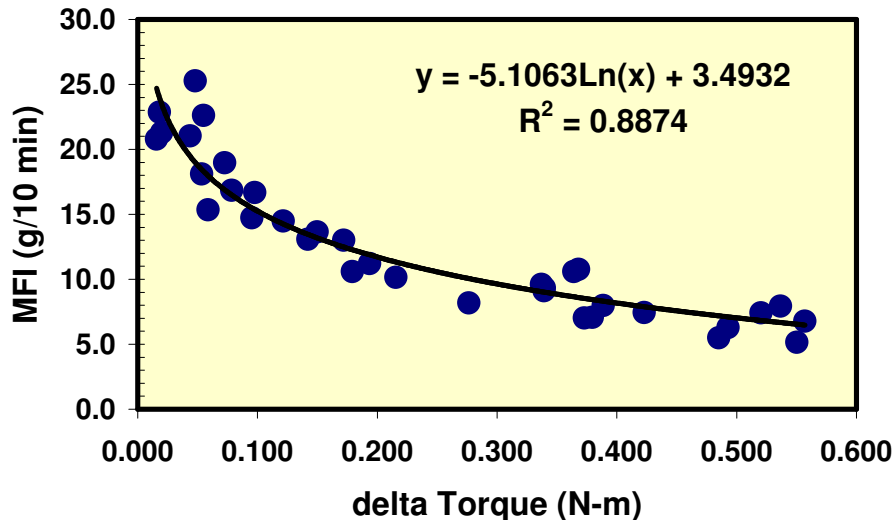
Another series of PP materials was made with a two-fold purpose: (1) determine how well the above relationship would predict the MFI's measured from the delta torque values and (2) evaluate a process using the two automated feeders with the microcompounder that could potentially be implemented to rapidly evaluate the effectiveness of new stabilizers, stabilizer combinations, and loadings. This series was designed with three different stabilized packages. Two of the packages were formulated into two PP masterbatches each at two different loadings. The third package was incorporated only into one PP materbatch. Each of the masterbatches were loaded into one of the feeders at a time and the second feeder contained unstabilized PP. The feeders were programmed to operate in relative ratios of 100/0, 75/25, 50/50, 25/75, and 0/100 in a random order but still running 100% unstabilized PP between each run containing stabilized material. Using this technique a wide range of stabilization levels of PP could be made (and a corresponding large range of MFI's) and a wide range of stabilization loadings could be accessed. The total run time for each composition was seven minutes with only the last two minutes used for torque data collection. The torque values for the unstabilized PP material before and after each composition were averaged and subtracted from the averaged torque values for the stabilized materials in the last two minutes.

These delta torque values were used in the equation listed in **Figure 39** to calculate the "predicted MFI" and compared to the historical MFI data obtained for these compositions prepared in the microcompounder over the course of the project. As can be seen in **Figure 40**, good predictive value is obtained. Only two points appear at the limits of the prediction interval

and can be considered outliers. Looking over the data, at least one of the points can clearly be identified as an outlier since it is one of the mid-range loading samples and is clearly different from the trend expected for the other materials in the series. This study clearly indicates that on-line torque measurements can be used in place of the long, laborious MFI measurements.

Figure 40. Relationship of MFI predicted from delta torque measurements versus historical values obtained for these materials prepared in the microcompounder.
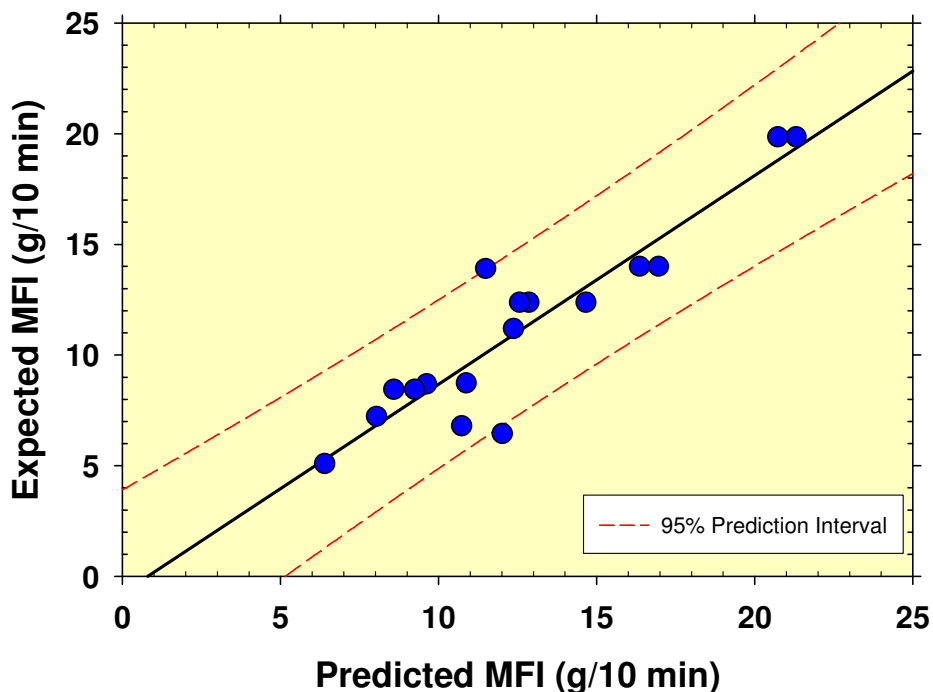
Extruded pellet melt behavior for MFI determinations

The ability of the method of observing the pellet melt behavior to differentiate stabilizer effectivenss was evaluated in the following manner. Three series of PP compositions containing different levels and types of stabilizers were run under the standard abusive conditions outlined in Task 4. The MFI's for these materials was measured and three pellets of each material were measured using the delta length technique outlined in Task 3.1. The pellets were trimmed with a razor before the initial measurement and then place on a microscope glass slide that had been sprayed with PTFE release. The pellets were then placed on a hot stage for 45 s, removed and their length re-measured. The relationship of the length change to the measured MFI's are shown in **Figure 41**. There is clearly a strong relationship indicated but a high degree of scatter exists no doubt resulting from the high variability in the measurement discussed in Task 3.1. Clearly, this technique could be used to screen high perofrmance stabilizers from poor performers. More rapid analysis is needed for a combinatorial methodology – this might be acheivable along with lower variability by incorporating an automated image analysis system.

Figure 41. Relationship of change in pellet length on melting at 300 C vs MFI

Chemiluminescence imaging of thermooxidative stability of materials arrays
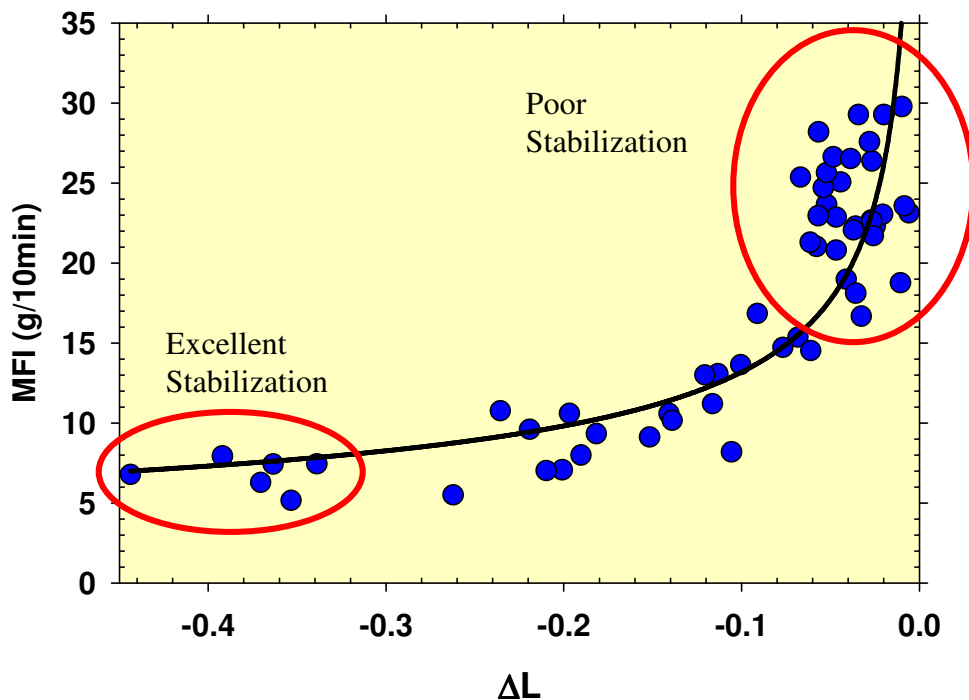
Numerous validation experiments were performed with arrays of polymers that were heated and the CL was collected in real time over a predetermined time of about 2 h. During these experiments, a set of images was collected. Upon completion, the images were analyzed

Figure 42. Illustration of a typical experiment of chemoluminescence imaging of thermooxidative stability of polymers. (A) An images from a kinetic series during thermal oxidation of polymer array containing materials 1 – 3 (1 – most stabilized, 3 – least stabilized). (B) Results of analysis of kinetic data.
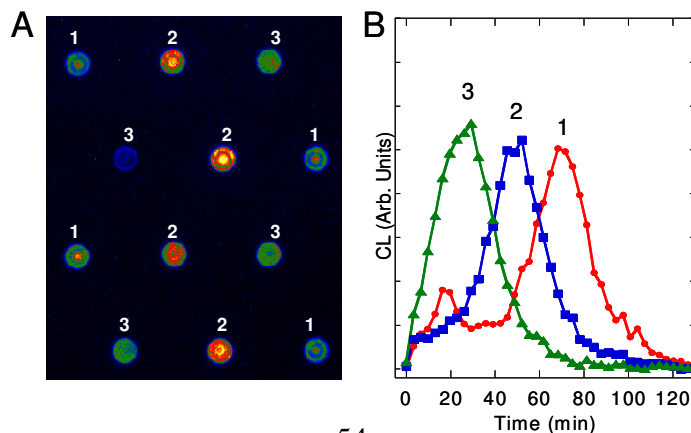
to extract the relevant kinetic data from the regions of interest. A typical image from a one of the experiments and the kinetic experimental profiles are illustrated in **Figure 42**. This data illustrates that the kinetic CL profiles are related to the stabilization efficiency of the polymers. However, in the process of continuing these studies, our literature review revealed that ranking of polymer oxidative stability as a function of different additives has not been reported in the literature to the level of detail to enable it to be used as a reference method [67]. Literature reports have focused on the chemoluminescence imaging of polypropylene samples under different oxyen environments and thermooxidation temperatues. Thus, the unavailability of a reference method made chemoluminescence imaging of polymers with different types of stabilizers less attractive since there was no way to reference the chemoluminescence behavior to the degree of stability imparted by each stabilizer.

Static dissipation measurements

The work to validate the static dissipation measurement is described in Task 3.1 along with the statistical measurements. The finding that the difference in static dissipation between polycarbonate with three loadings of anti-static agent is a strong indication that this method is valid. As this work was progressing, it was envisioned that a larger set of materials would be explored and add to the validation set. However, since this property was not one of the key properties identified in Task 1, it was decided not to expend this effort to broaden the validation set at this time.

Micro-biaxial impact measurements

A series of ABS materials were prepared with progressively increasing rubber loadings (0 to 25% rubber) thereby increasing ductility and decreasing modulus and yield strength. This series was extruded into films using a conventional scale extruder to prepare materials suitable for use in the micro-biaxial impact tester. These materials were also processed by conventional injection molding into 0.125" thick, 4" inch diameter disks for conventional instrumented dart impact testing. **Figure 43** shows the correlation of the impact energy obtained with the micro

Figure 43. Correlation of impact energy for ABS series in micro-biaxial test to that in conventional instrumented dropped dart testing.
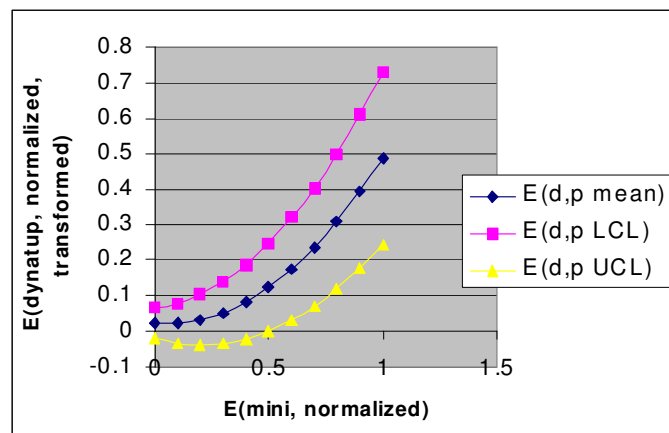
tester on the ABS series to that of conventional biaxial instrumented impact test, together with

95% confidence intervals around the relationship. The miniature biaxial test clearly allows similar ranking of materials within the series and perhaps slightly better discrimination between samples of very low impact energy than that afforded by conventional testing.

  Similar studies were also carried out with polycarbonate and polyetherimide series which contain materials of varying ductility. In the case of the polycarbonates, which have inherently high ductilities, ductility differences are small. However, the micro-biaxial impact test results indicate that this methodology may be able to distinguish these types of differences (**Figure 44**) and they appear to correlate with their notched Izod impact, an important polycarbonate test (**Figure 45**). The polyetherimides (**Figure 46**), in general have low ductilities, but are distinguishable from each other in conventional testing and correlate well with the energy

Figure 44. Micro-biaxial impact energies for polycarbonate series.
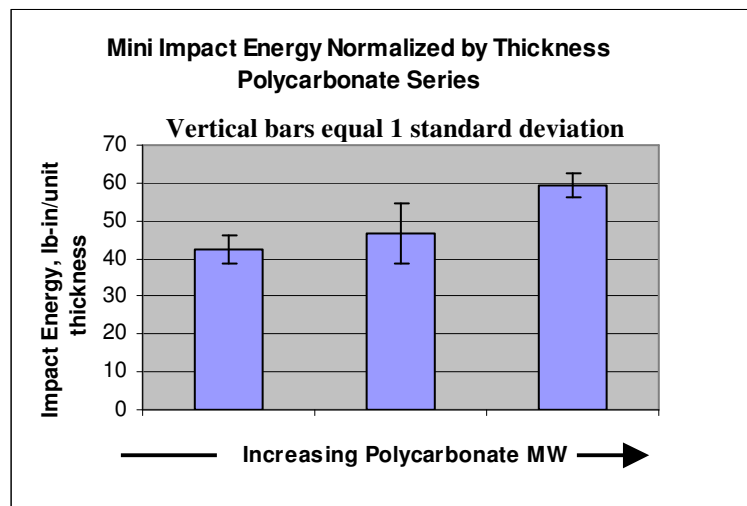
Figure 45. Conventional notched Izod impact vs micro-biaxial impact for polycarbonate resin series.
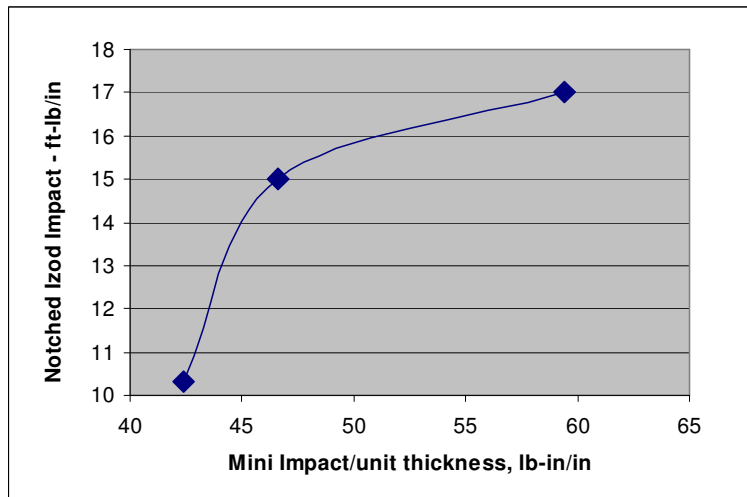
differences measured in the micro-biaxial test.

Figure 46. Conventional instrumented dart impact total energy versus micro-biaxial impact energy for polyetherimide series.
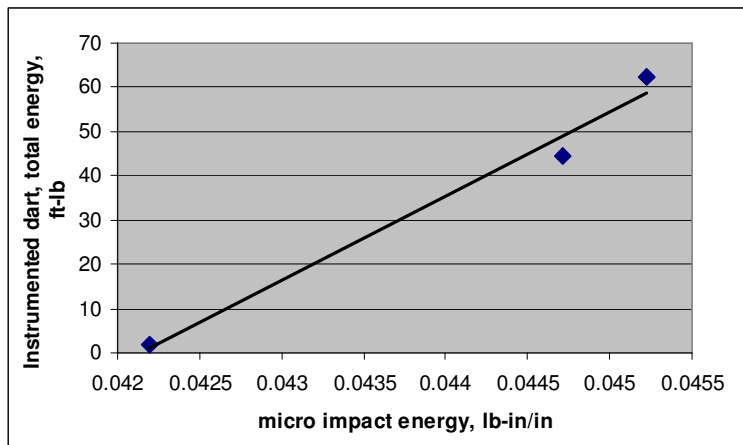
These results indicate that the micro-biaxial test can serve as an alternative to conventional testing. The material required per 10 impacts is ~ 1g, and the time per test is 1 minute, which compares favorably with ~ 1 kg and ~ 1hr for the equivalent quantities when conventional testing is performed.

Task 3.3—Perform instrument manufacturer needs mapping and requirements flowdown.

This task was accomplished by K-Tron, International as the commercialization sub-contractor.

Customer needs mapping

The intent here was to engage a statistically significant number of potential customers in the development of specifications for what was referred to as the "Combinatorial Microcompounding/High Throughput Screening Product Development Platform". A "Needs Mapping Document" and a potential customer list were developed. These were sent to the potential customers on the list. Follow-up phone calls were made to confirm receipt of the document, to clarify our intent and to elicit the cooperation of these potential customers. While the process was met with limited success, at least some information was gathered that was helpful in developing the engineering specifications necessary to define the product platform which can be subsequently developed and commercialized.

Needs mapping document

This document was comprised of three sections. Please refer to Attachment I. The first section was a vision statement which, in summary fashion, articulated a concept for a fully integrated product development platform that incorporated a microcompounder directly linked to microanalysis instrumentation.

The second section was designed to identify the potential customer and to develop an understanding of their current product development environment. Information on type, size and number of lab scale compounding equipment was requested. We also asked for details about the operation of this equipment in the course of their product development activities. Finally, we asked the potential customer to rank the five material properties and their method of measurement most important to their product development process.

The third, and most important section was designed to get the customer to think about an alternative to their current product development practice that would be based on a microcompounding/high throughput screening product development paradigm. We asked what such a system needed to look like to make it an attractive alternative to their current mode of operation. Questions focused on the microcompounding equipment, its operation and control and the need for systems integration, networking and data management. Microanalyses needs were explored in terms of properties measured, number of properties necessary to rank developmental resins and ability to accommodate rapid off-line analysis (for cases where on-line analysis is not available). Finally, a series of questions were asked to quantify the value of such a system as a function of its technical, operational and economic attributes.

Potential customers and their contact

Potential customers were selected from four market segments defined as follows:
1.   Major polymer resin producers
2.   Large-to-medium specialty compounders
3.   Small/entrepreneurial enterprises
4.   Academic institutions

The list of 22 candidates identified heavily favored the first two market segments with only minor representation in the last two market segments. Contacts were key technical stakeholders in their respective organizations. Since confidentiality was assured at the onset, names of organizations and individuals cannot be identified.

The initial mailing was issued in September of 2002. The "Needs Mapping Document" was sent under a cover letter (refer to Attachment II). The letter attempted to 1) introduce combinatorial/microanalytical methods and its potential application to polymer resin product development, 2) describe the nature of this DOE-funded project and K-Tron's role in this project, and 3) request their participation in the customer needs mapping process. Follow-up phone calls were made to confirm receipt of the document, to clarify our intent and to further elicit their participation.

Customer responses

Overall, the response was disappointing. Only one potential customer responded to the first mailing/phone campaign. A second mailing/phone campaign was executed beginning in January of 2003. This started out more promising with several commitments to participate. But only two additional potential customers finally responded for a total of 3 responses out of 22 inquiries. That's a 13.6% response rate. Perhaps this is not a bad rate as surveys in general go, but it makes for a rather small database from which to develop engineering specifications.

Some commentary seems appropriate. The reason does not appear to be a lack of interest or low-perceived value in this new technology. Rather, other factors appear to come into play. Most of these potential customers are competitors; between themselves and certainly

with GE (the major contractor in this project). In the process of discussions with the potential customers, this topic almost invariably was cited as a concern. In at least some of our discussions, it was made clear that these people and their organizations were very busy and would not have time to participate in this needs mapping process. Indeed, some of the unfilled promises to participate were due to this factor. Finally, in some cases, for unknown reasons, potential customers refused to return calls. Perhaps in these cases it was concern over confidentiality, schedules already too full, or little interest in participating in the development of a concept that might only someday be realized commercially.

Of the three responses that were secured, two came from major polymer resin producers and the third came from an academic institution well known in the polymer science and engineering community. So, while the response was limited, it represents inputs from the most important commercial market segment and from the small, but nevertheless important academic market. The actual responses are contained in Attachments III, IV and V.

Customer needs – the current environment

All responders have lab scale compounding lines utilizing single screw extruders up to a screw diameter of 1 ¼-inch and co- and counter-rotating twin screw extruders with a screw diameter up to 34mm.   In one case a kneader is also used. Total extruder throughput ranges between 1 and 200 lb/hr. Feeders are invariably used with 2 to 4 per extrusion line. Individual feeder rates span a range of 2.6 to 100 lb/hr. In the process of generating developmental formulations batch size ranges from 1 to 50 lb. with the number of batches run per day ranging from 1 to 20.

In all cases, compounded product properties are measured by standard methods off-line. In all cases, some measure of melt rheology (e.g., MFI, melt viscosity) and mechanical properties (e.g., tensile, flexural, impact) are measured. In two cases, some measure of dispersion is made and color is measured. Finally, for certain responders, dynamic mechanical, thermal and specific growth determination is conducted.

Customer needs – future microcompounding/high throughput screening product development system

The microcompounding line favored is a co-rotating twin screw extruder. The industrial responders specified a minimum throughput rate from 0.5 to 2 lb/hr and a maximum throughput rate of 5 to 10 lb/hr. The academic responder specified a range from a "technically limited" minimum to a maximum rate of only 1 lb/hr. In all cases an extruder equipped with segmented screws and split-barrel capability was specified.

The extruders should be equipped with between 1 to 3 feeders which can feed powder, flake and pellet feedstocks. Industrial lab installations call for feed rate minimum of 0.5 to 2 lb/hr and maximum feed rates of 2 to 10 lb/hr. The academic application specifies minimum and maximum federates of 0.1 and 0.9 lb/hr, respectively. Finally, in two cases, liquid feeding capability was also requested. And, the low rates of the academic application suggest feedstock grinder be supplied to reduce particle size to a range appropriate for very low rate feeding.

In two cases integration to a laboratory automation management system is desired, e.g., to a product development database. In terms of data management , Excel spreadsheet software is preferred.

The required microanalysis reflects current property measurement practices. In all cases some measure of melt rheological, mechanical properties and color are specified. In selected cases dispersion, compositional analysis and thermal properties are important. In other cases certain end use properties like flammability, weatherability, and static dissipation are also specified.

Most important for on-line analysis are rheological properties, dispersion analyses, color and composition. Acceptable for off-line analyses are physical, thermal, mechanical, dynamic mechanical and advanced chemical analyses.

Customer needs – value proposition

In all cases increased productivity is a great value adder to polymer resin development. The industrial responders would find it attractive to adopt the microcompounding/high throughput screening product development paradigm if they could realize a 5X to 10X productivity gain. The academic party saw value with only a 2X productivity gain.

Attributes like accuracy, system reliability, expandability, adaptability and automation, the ability to manually operate and ease of use drive the justification to purchase.   The equipment should be smaller in size than current equipment. In one case a table-top system with a 4-foot by 3-foot footprint was cited as attractive. In only one case was potential system cost commented upon; at $85,000 they would "buy it today"; at $150,000 they would put it in the budget and at $200,000 it would be too expensive.

Task 3.4—Develop methodology for integration of microanalytical techniques with microcompounding equipment

The efforts and results concerning this task are contained in the discussion of the validation of the various methods in Task 3.2 as well as in the discussions in Task 4. Overall, it was shown that in-line measurements using spectroscopic methods and measurements of screw torque are feasible at the scale and rate of the current microcompounder (10-30 g/min and a strand diameter of ca 1 –1.5 mm). For spectroscopic measurements, a in-die or strand holding device would need to be designed to insure that the probe is maintained in a regular configuration relative to the sample.

The preparation of materials in film form requires additional work direct toward significant modification of the microcompounding equipment. Primarily to enable a broader processing range and better control of film thickness uniformity and width. Although it is possible that methods utilizing film samples, such as the electrostatic measurements and micro-biaxial impact test, could be configured to operate on the film in-line as they are produced, it is preferred that these be off-line tests so that environmental conditions (temperature and humidty) can be more easily controlled. In addition, testing off-line from the microcompounder eliminates the need to match the output speed of the microcompounder with the testing speed.

For film and also for strand, off-line tests using a coiled sample configuration in which the microcommpounder continuous output with varying composition is collected around a coiled mandrel is particularly attractive. We have demonstrated this fully in one test that is discussed in Task 4.3. This sample collection approach allows for continuous off-line measurement on the fully coiled material as an array as well as an uncoiled sequential feed into the testing device (as described for the micro-biaxial impact tester in Task 2.3). Either manual coiling or crude automated coiling were used in this program to demonstrate the concept. Additional

mechanical design is required to implement these concepts although such devices are typically used in larger scale commercial devices.

In order to make the preparation of gradient arrays as flexible as possible, the incorporation of at least three materials feeders is needed. Although this is possible in the microcompounder we used, a different configuration where the feed port is more openly accessible would improve the ability to add additional feeders as required.

Task 3.5—Develop design specification for commercial instrument(s)

Based on the results of the microanalytical methods development and the customer needs mapping, a preliminary design specification was written by K-Tron for a Combinatorial Microcompounding High Throughput Screening Porduct Development Platform(CSS). The detailed document is included as Attachment VI.

The device will consist of an extruder, feed system, computer control and data collection system with various in-line and off-line analysis systems based upon the methods developed in this project.

Task 4—Develop Advanced Microcompounding Techniques for Preparation of Polymer + Additive Formulations

Task 4.1—Demonstrate Proof of Concept for Rapid Preparation of Polymer + Additive Formulations via Microcompounding

Prior to the start of this project, although micro-scale compounders had been available for a few years, there was little information describing the operational parameters needed to prepare materials in such devices. This task was focused on exploring the basic process conditions for operating the micro-compounder, developing baseline operating conditions for processing both film and strand (feeding, compounder screw speed, and compounder barrel temperature, etc) and modifying or obtaining equipment to facilitate these operations. The materials primarily used for these baseline studies were polypropylene and polycarbonate.

We investigated the possibilities of continuously feeding resin into the micro-compounder. Initially, various simple, semi-manual devices were used to add material in a regular, semi-continuous fashion to the extruder. Subsequently, simple vibratory and screw feed mechanism were constructed and evaluated. These devices, although capable of continuous feed, proved to be unreliable in delivering consistent feed rates especially on a day-to-day basis without constant recalibration. Similarly, a small commercial vibratory feeder provided a good range of addition rates but proved difficult to re-set and to obtain the same rates on repeated runs. After substantial work with these various devices, which afforded us the opportunity to understand the basic operation of the microcompounder, a prototype commercial micro loss-in-weight feeder was obtained from K-Tron International.

Work with the microfeeder showed that addition rates could be obtained which ranged from a high of 12-13 g/min for PC powder and 35-40 g/min for PP powder to a low of ca 2 g/min for each material. For a feedrate of 10 g/min of PP, this feeder typically delivered within 3% of the setpoint for sample collected for over a 1 min span. We subsequently obtained a second identical feeder and connnected both feeders' control systems to a PC via LabView software. The PC not only logged the output data from the feeders but enabled us to automate the control

of the feeders to create rapid changes in discrete compositions as well as to make gradient arrays. A demonstration example of one of these arrays is shown in **Figure 47**, where feeds of two dyed PP materials were used. The automated operation of the two feeders was used to prepare the series of stabilized blends with multiple stabilizers and loadings used in the torque-MFI studies discussed in Task 3.2. Very late in the program, we also obtained a third loss-in-weight microfeeder from K-Tron. It was envisioned that with three three automated feeders, ternary gradient blends could be made and a series of stabilized PP formulations could be evaluated and optimized using the microcompounder torque technique three to five times more rapidly than with traditional methods. A picture of the configuration of the two feeders and the microcompounder, waterbath, and pelletizer is shown in **Figure 48**.

Figure 48. Picture of gradient of two dyed PP formulations. Gradient was changed in 20% increments every 30 s at a total feed rate of 10 g/min.
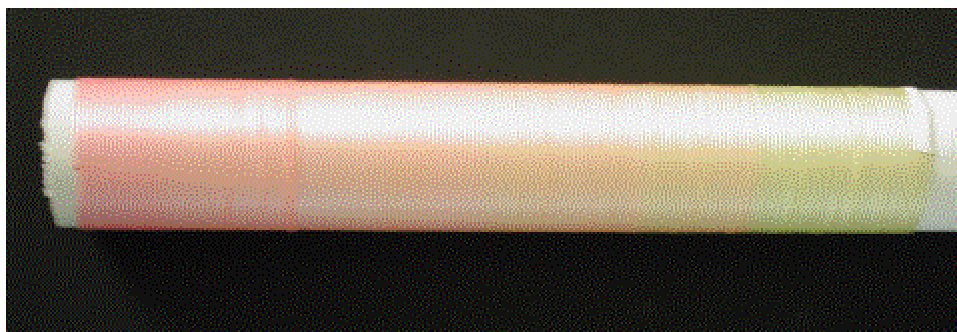
A low feedrate of only 2-3 g/min was found to be necessary to prepare good quality films with the microcompounder under any conditions for PP or PC. One potential area for additional

Figure 47. Microcompounder with two loss-in-weight feeders, water bath, and pelletizer.

work may be re-design of the film die to enable production of films using higher feedrates (and throughputs). Tests such as the micro-biaxial impact testing, static dissipation, and potentially micro/nano indenting, require films with good thickness uniformity and widths of 10-25 mm. We had significant difficulty with the current microcompounder consistently making films with those properties. In addition, the ability to make array compositions in films currently requires being able to make films at a feedrate reasonable for the feeders (10-20 g/min total feed rates from all the feeders). The design limitation of the current microcompounder may require a new microcompounder device to overcome these issues for film production.

Under appropriate microcompounder screw speeds and temperatures, strands could be easily processed for a whole range of feedrates in the microfeeder with PP. Indications are that if higher feedrates are possible, even greater throughputs through the microcompounder might be attained. However, PC powder was more difficult to process in the microcompounder and flood feed conditions were obtained with feed rates near the maximum feedrates of the microfeeder.

In order to increase our ability to process various forms of microcompounder output, a waterbath (for cooling molten output) and winder (for collecting intact film or strand) were constructed in-house and a small chopper (for pelletizing strand for use in traditional base-line melt flow measurements) was obtained from the GE Research polymer processing laboratory (**Figure 48**). Similarly, modifications were made to the feed funnel of the microcompounder to reduce pre-melting of the resin in the funnel allowing for easy feed to the compounder. A data collection program was written to monitor and record both microcompounder conditions and feed rate data in real time.

Early experiments were also conducted to explore the ability of the microcompounder to adequately disperse materials representative in size to additives such as stabilizers. These experiments were performed using PC powder blended with ca 0.01 phr (parts per hundred resin) dye or pigment. Each PC mixture was compounded using batch conditions with ca 3.5 g charge of the mixture added over 2 minutes with an additional mixing time of 2 minutes in which the melt was recirculated back through the barrel before collecting the output in the form of a film. Similarly, the same compositions were starve-fed to the microcompounder operating in continuous mode (no recirculation) and collected immediately as film. Microscope images of the collected products show the dye to be well dispersed with no gross differences in the quality of the mixing or dispersion between the two process conditions. Examples of the comparison materials are shown in **Figures 49** and **50**.

Figure 49. Dispersion for continuous, single pass compounding.
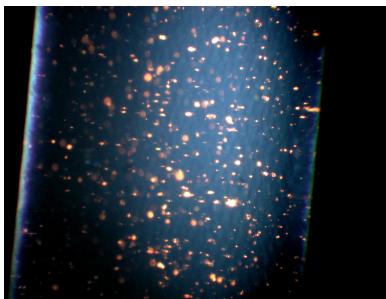
Figure 50. Dispersion for batch, 2 minutes re-circulation compounding.
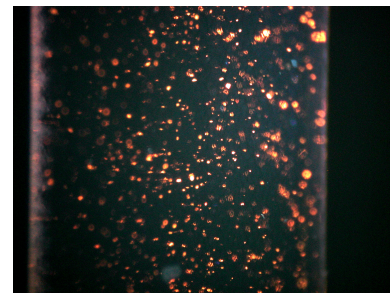
One of our initial areas, identified in the QFD cited in Task 1, was to explore conditions under which process stabilizers for polyolefins such as polypropylene could be evaluated. The efficacy of a process stabilizer system is often evaluated using the technique of multi-pass extrusion [68-76]. The polymer and stabilizers are subjected to four or more consecutive passes through an extruder and physical properties of interest are measured on samples taken from each pass. Those stabilizers that maximize retention of performance properties with successive passes are judged to be most effective. In the case of polypropylene, the primary physical properties that are usually evaluated during multi-pass extrusion are MFI and YI [76]. **Figure 51** demonstrates the typical change in melt flow with conventional multi-pass extrusion (in a 1.5" diameter single screw extruder) of a PP with nominal initial MFI of 4 g/10min.

Our first step was to demonstrate that PP degradation (as shown by the method of observing an increase in melt flow index) could be induced in the microcompounder. Various conditions of barrel temperature and screw speed were explored and the resulting changes in melt flow were measured. As indicated in **Figure 52**, under select conditions, a single pass in the microcompounder can result in increased MFI (corresponding to the amount of degradation) similar to the increases in MFI obtained in the multiple pass extrusion method in a conventional

Figure 51. MFI shift for typical conventional multi-pass extrusion. Pass 0 is a compounding pass at 230 C under argon atmosphere. Passes 1-5 are at 260 °C in air.
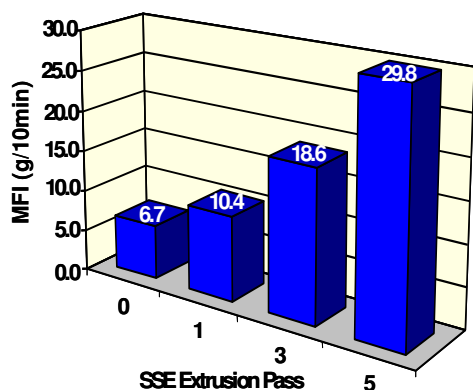
Figure 52. MFI shift for single pass extrusion in micro-extruder with 2 g/min feed rate as a function of temperature and screw speed
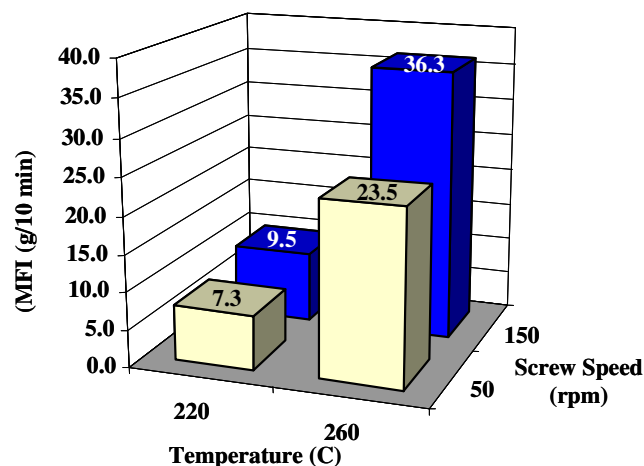
extruder. This result indicated a possibility for optimization of the microcompounder conditions that could initiate significant degradation in PP in a single pass that would provide the same rank order of stabilizer efficacy as the conventional multiple pass single screw extrusion protocol [36].

Task 4.2—Identify Key Operating Parameters for Preparation of Polymer + Additives in a Microcompounder

A screening design of experiments was conducted to obtain a better understanding of the influence of the microcompounder process conditions on the MFI shift of PP. The complete eight run design, which used unstabilized PP with 500 ppm calcium stearate, was fully replicated on a second day and samples from each of the 16 runs were taken for MFI measurements. The results of these experiments are depicted in **Figure 53**. Each vertex in the

Figure 53. MFI results for 2^3 factorial DoE for micro-extruder process variables with PP containing 500 ppm calcium stearate. Pairs of values at each vertex are the MFI's for replicate runs.
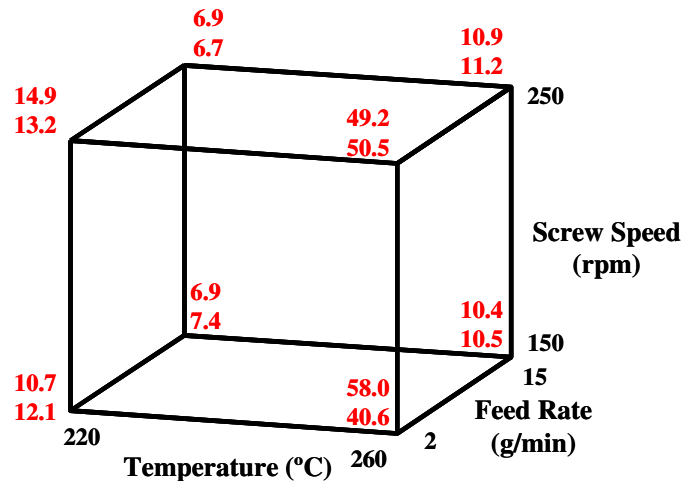
experimental design cube contains MFI values representing the replicates for each condition. One of the conditions (260 °C, 2 g/min feed rate and 150 rpm) had a large difference between the MFI's for the duplicate runs - due to the lack of material, repeat analysis could not be performed to check this discrepancy.

These experiments demonstrated that higher barrel temperature and lower feed rates in the microcompounder increase MFI's while the screw speed has essentially no effect. The range of MFI's along the high temperature face of the experimental design cube indicates that it should be possible to run at a moderate feed rate at ≥260 °C in the microcompounder and induce PP degradation similar to that obtained after the fifth pass at 260 °C in the multi-pass experiment.

At this time, we also evaluated the effect of the microcompounder process conditions on the residence time distribution. As described in the extrusion literature [77-81], feed rate (mass flow) and screw speed have strong effects on the residence time distribution and these effects are also seen in the microcompounder as shown in **Figure 54**. For these experiments a small (mg) amount of a fluorophore-impregnated PP powder, was added to the continuous feed stream of virgin PP powder fed to the microcompounder at the noted feedrates. The feed rate obviously has the strongest effect – but increasing screw speed does lead to a narrower distribution with a shorter time to peak residence time. The very broad distribution obtained at the lowest feed rates could result in difficulty obtaining consistent results and product distributions and could necessitate very long run times. Therefore, higher feed rates appear to be more desirable as long as sufficient mixing can be obtained.

Subsequently, a set of follow-up central composite designs of experiments were

**Figure 54. Residence time distributions for various rpm and feed rates at 260 °C barrel
temperature in the microcompounder.**
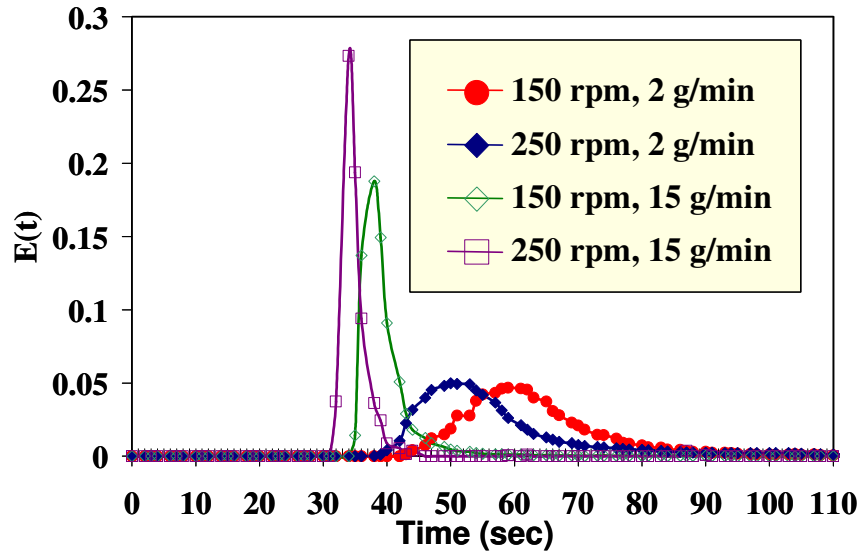
conducted to understand the day-to-day/operator effects and to further optimize the temperature
and feed rate of PP in the microcompounder to induce a large shift in PP melt flow from the
nominal 4 g/10min to ca 18-20 g/min in a one pass continuous feed operation. The variables
were barrel temperature and feed rate with the screw speed held constant at 150 rpm. Although
statistically significant, the day-to-day/operator effects were found to be small compared to the
effects of temperature and feedrate. As shown in **Figure 55**, melt flows of >18 g/10min were

**Figure 55. Central composite DoE results for temperature and feed rate effects on PP
MFI shift in microcompounder. (Contour lines = MFI in g/10 min).**
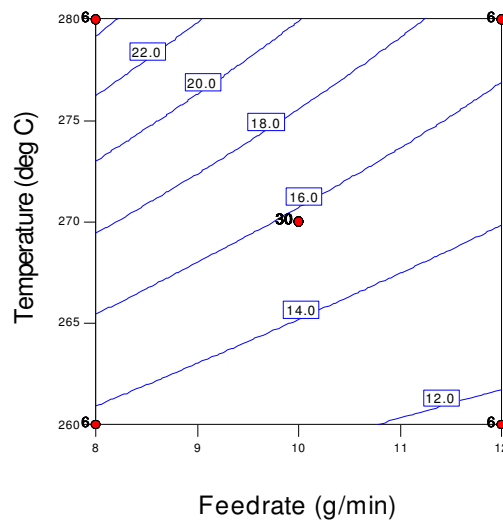
obtained at temperatures of 270 C or above at the selected range of feed rates (8-12 g/min). This range of feed rates represent reasonable areas of operability for our loss-in-weight weight feeder. In particular, a feed rate of 10 g/min represents a good overall target feed rate and as a result these experiments lead us to select a standard operating condition for PP process stabilizer evaluations in the microcompounder of 280 C and 10 g/min (with 150 rpm screw speed).

Task 4.3—Validate Microcompounder Capability

Two sets of experiments were further performed to test the potential of using the microcompounder to accurately predict the rank order efficacy of stabilizers in PP. In the initial experiment, four stabilized PP compositions along with the unstabilized PP starting material were subjected to both the multiple pass protocol and a single pass in the microcompounder (8 g/min, 260 °C, and 150 rpm) with both sets of materials evaluated by the traditional melt flow method. As shown in **Figure 56**, the MFI from the fifth pass of the traditional multi-pass experiment correlates quite well with the microcompounder MFI. This data demonstrated that it is possible to use the microcompounder to predict the rank order of PP stabilization obtained in a conventional multi-pass experiment in a larger extruder.[36]

Figure 56. Correlation of melt flows from 5th passes of conventional multiple pass tests with single pass microcompounder protocol. Initial limited sample set.
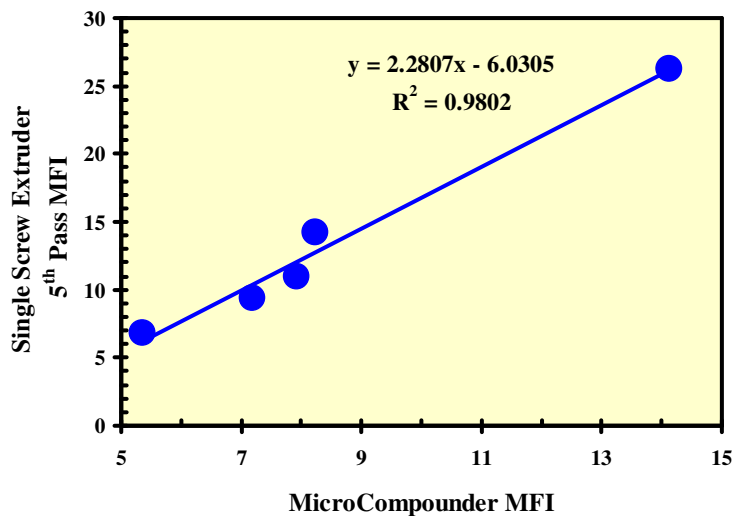
The original sample set for the correlation study was relatively small, and was run prior to the analysis of the design of experiments optimizing the degradation conditions. The stabilizers systems used were all good to excellent in effectiveness so although the correlation was good there was a large gap between the lower melt flows and the higher melt flow obtained for the unstabilized resin. A second correlation study was performed with a larger number of stabilizer systems chosen so that a more uniform distribution of stabilization effectiveness would be obtained, and with process conditions of 10 g/min, 280 C barrel temperature and 150 RPM screw speed. Although more scatter is seen in this data set, **Figure 57** shows that there is still

a very good correlation between the rank order of PP degradation obtained from the fifth pass of the conventional multiple pass experiment and the single pass microcompounder experiment.

The validation of our ability to induce the same rank ordering for PP degradation (stabilization effectiveness) obtained in a the conventional multi-pass extrusion and MFI testing but using specific conditions in the microcompounder forms the basis for the subsequent microcompounder conditions used in exploring the torque, pellet melting, and spectroscopic analysis methods with either single feed or binary feed compositions (where the sum of the feed rates of the two feeders is set to keep a steady 10 g/min feedrate).

Figure 57. Correlation of melt flows from 5th passes of conventional multiple pass tests with single pass microcompounder protocol. Expanded sample set.
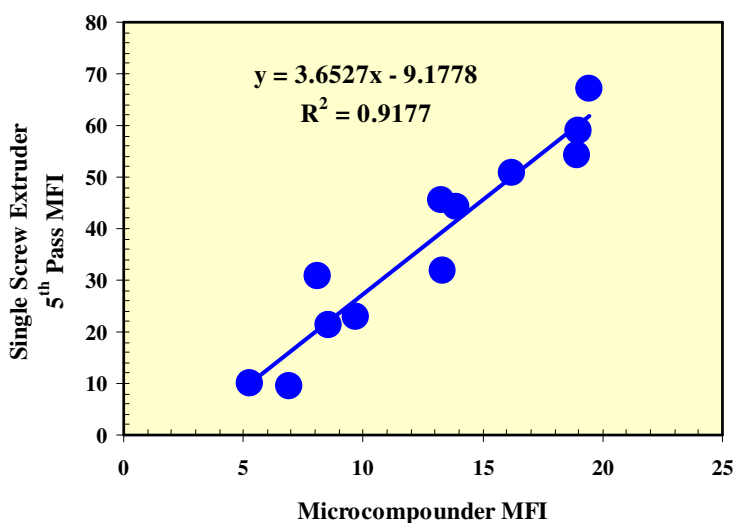
The capabilities of the microcompounder equipped with multiple feeders to produce 1-D compositional libraries was also demonstrated in a combinatorial study of weathering performance in polycarbonates.[82]. Here two polycarbonate masterbatches were used. Each masterbatch contained 1% TiO_2 while one also contained 2% Tinuvin 234 UV stabilizer. A continuous strand of polycarbonate with different concentration of Tinuvin along its length was made by extruding the two polycarbonate masterbatches at different ratios of feedrates for the microfeeders while maintaining a constant overall feedrate of 8 g/min and operating the microcompounder at 150 rpm screw speed. By changing the ratio of the feeders, TiO_2 - pigmented polycarbonate compositions containing 0, 0.6, 1.0, 1.4, and 2 wt% UV absorber were extruded as a ca 1 mm diameter strand. This material was then coiled around a cylindrical mandrel and exposed in a Xe-arc Weatherometer (Atlas Model Ci35A) at a overall exposure dose (at 340 nm) from 170 to 845 kJ/m^2.

Fluorescence measurements of the coiled 1-D libraries were performed periodically during weathering using automated fluorescence imaging and spectroscopic systems. Fluorescence imaging permits rapid evaluation of all regions of 1-D libraries with adequate

signal-to-noise and spatial resolution. As an example, **Figure 58a** depicts white light and fluorescence images of one of the 1-D libraries after 845 kJ m-2 exposure. These images illustrate that it is possible to resolve individual coils in the weathered materials array. Also, knowing the locations of the coils from the white-light image, it is straightforward to correct for any intensity differences in a fluorescence image. Using an automatic scanning fluorescence spectroscopic system, in which a fiber-optic probe moved across the coiled library the fluorescence was recorded as a function of traveled distance, we obtained information about the weathering, as shown in **Figure 58b**. At the initial stage before weathering, the library regions with the UV absorber had slightly elevated fluorescence intensity, and upon weathering, the rate of fluorescence increase of the UV-stabilized regions was less than that of the regions without the UV absorber. A comparison of fluorescence for different concentrations of T234 and different weathering conditions is presented in **Figure 58c**. Fluorescence intensity was dependent on both the exposure dose and the level of T234 UV absorber in the polymer formulation. This plot also shows that fluorescence intensity of coiled regions before weathering slightly increases as a function of T234 UV absorber. However, upon weathering, the rate of fluorescence increase is reduced by the UV absorber. This rate reduction is proportional to the concentration of UV absorber in the polymer.

Figure 58. Demonstration of performance testing of 1-D libraries of polymer compositions. (a) White light and fluorescence images of a 1-D library after 845-kJ m-2 exposure. (b) Spatially resolved fluorescence profiles of the 1-D library at increasing levels of exposure dose. (c) Weathering response of the 1-D library of polymeric compositions containing increasing amounts of UV absorber T234 at increasing levels of weathering exposure.
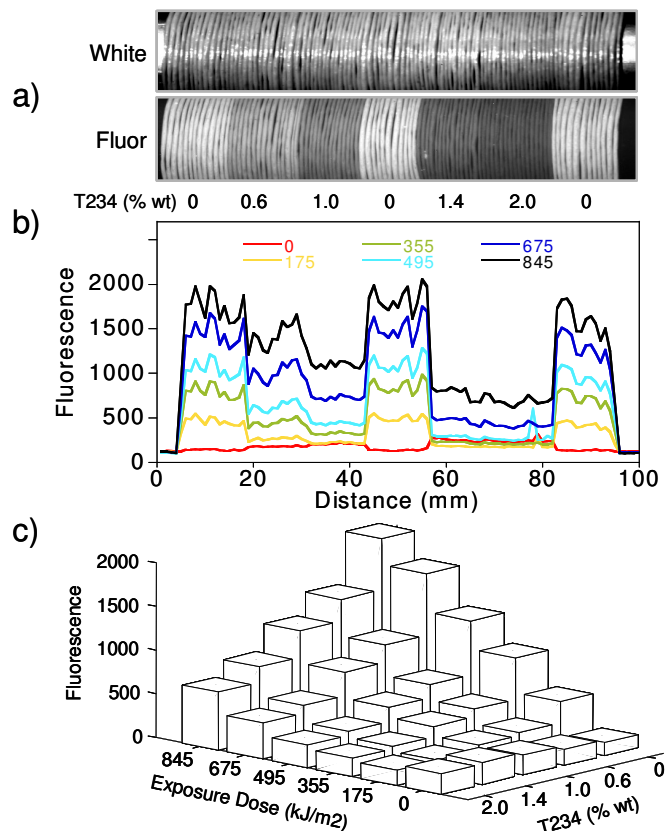
Task 5—Generate technology commercialization plan

Product platform development

The Combinatorial Microcompounding/High Throughput Screening Product Development platform will be developed in three phases, ultimately resulting in a three-tier product offering. These product tiers are:

1.   Polymer/Additive Systems (Tier 1)
2.   Polymer/Polymer Systems (Tier 2)
3.   Reactive Compounded Systems (Tier 3)

Each tier will be developed and realized commercially based on the availability of necessary enabling technologies. These include:

1.   Microcompounding Capability
2.   Compounded Product Microanalyses
3.   Control and Networking Requirements

Tier 1: Polymer/additive systems

Development of a Tier 1 product development platform for relatively simple polymer/additive systems (which is the focus of this project) will be the first to be realized. The extrusion compounding of additives in a simple polymer is well established and seldom wrought with complications. Extruder/screw configurations typically have broad applications at the laboratory scale, and results are the most easily scaled up to larger machines (e.g., pilot plant and up to small manufacturing line).

The goals of resin development for these systems most often include stabilization (e.g., heat, ultraviolet light, weatherability), rheological modification (e.g., MFI), resistance to environmental stresses (e.g., flammability) and appearance attributes (e.g., color, gloss). The measurement of these performance parameters can be accomplished, even in an on-line microanalysis mode, by commercially available instruments or by commercial equipment currently in the latter stages of development. The former include on-line rheometrics while the latter includes IR and UV spectrometers as well as melt color monitors, all in on-line configuration suitable for microanalytic procedures. Physical, thermal, mechanical, dynamic mechanical properties and advanced chemical analyses can be handled off-line directly using small/micro sample methods that are currently available or under development.

Formulation libraries can be generated by the use of existing combinatorial methods and/or design of experiments methods. The same packages can also be used for the compilation of a results library as well as providing appropriate search engines. These features will be an integral part of the overall control and networking systems necessary to manage the effective operation of this product development platform.

Tier 2 and Tier 3: Polymer/Polymer and Reactive compounded systems

The development of Tier 2 and Tier 3 product development platforms will follow the realization of the Tier 1 offering. These more advanced platforms will need to accommodate far

more demanding compounding operations, and more sophisticated and complex analytical methods.

For microcompounding of polymer/polymer (Tier 2) and reactive compounding (Tier 3) systems, the screw design, process configuration and process operation are very often specific to the resin system under development. Moreover, these process parameters are not easy to define apriori and successful designs often are a result of an interactive trial and error process. Multiple feed ports with multiple feeders at each port are not uncommon. For at least some cases, the very low feed rates required for certain additives, reactive agents or catalysts will challenge current feeding and weighing technologies. Microcompounding system flexibility will be required to achieve success in generating relevant resin formulations.

Analogous complications arise with respect to the analysis of compounded resin formulations resulting from Tier 2 and Tier 3 product development. For these resin systems, properties are far from simply dependent on formulation. Indeed, the polymer blend morphology, the deformational mechanics, and specific chemical reactions are tightly coupled to process parameters (screw design, process configuration, operating conditions) and strongly influence the properties of the compounded resins. So, to be successful, it is very probable that experimental matrices will have to grow in size to include both resin formulations and the appropriate process parameters. While this may not have a large effect on the microanalysis of compounded products per se, it will certainly make more difficult the work to correlate results from on-line microanalysis to real engineering properties, especially when selecting candidates for scale-up activities.

Product development platforms for polymer/polymer (Tier 2) and reactive compounded (Tier 3) systems are not the focus of this project. But success here will be dependent on the learnings garnered from the development and commercialization of the more simple Tier 1 product development platform focused on the much simpler polymer/additive resin systems.

Patents

Six patent disclosures have been submitted into the GE system for inventions developed on this project. No filings have been made at this time.

Publications

R. J. Wroczynski, *Accelerated Characterization of Polymer Properties,* Presentation at OIT-sponsored session at AIChE Spring Meeting in New Orleans on March 12, **2002**.

R. A. Potyrailo, *Development of High Throughput Analysis Infrastructure For Combinatorial Materials Science Applications*, Presentation at Pittcon **2002**, March 17 - 22, New Orleans, LA

Wroczynski, R. J.; Potyrailo, R. A.; Rubinsztajn, M.; Enlow, W. P. *Micro-scale extrusion for the accelerated development of new polymeric materials*, ANTEC **2002** - Proceedings of the 60th Annual Technical Conference & Exhibition, Vol. XLVIII, San Francisco, CA, May 5 – 9. Society of Plastics Engineers, pp. 2737-2771

Potyrailo, R. A., Wroczynski, R. J., Morris, W. G. *High-Throughput Analysis of Polymer Properties Using An Acoustic-Wave Transducer System*, Eurosensors XVI, Prague, Czech Republic, September, **2002**.

Potyrailo, R. A., Wroczynski, R. J., Rubinsztajn, M. *Spectroscopic Sensors for Determination Oxidative Stability of Extruded Polymers*, Eurosensors XVI, Prague, Czech Republic, September, **2002**.

Potyrailo, R. A., Wroczynski, R. J., Morris, W. G. Bradtke, G.R. *Determination of Oxidative Stability of Polymers Using Chemical Sensors*, Proceedings of the 9th International Meeting on Chemical Sensors, Boston, MA.

Potyrailo, R. A., Wroczynski, R. J., Pickett, J. A., Rubinsztajn, *High-Throughput Fabrication, Performance Testing, and Characterization of One-Dimensional Libraries of Polymeric Compositions*, M. Macromol. Rapid. Commun., **2003**, *24*, 123-130.

Potyrailo, R. A. *Sensor arrays for high-throughput design, performance testing, and characterization of complex materials*, COMBI 2003 - The 5th Annual International Symposium on Combinatorial Approaches for New Materials Discovery, February 19 - 21, San Jose, CA, **2003**.

Potyrailo, R. A.; Wroczynski, R. J.; Rubinsztajn, M. *Spectroscopic tools for high-throughput analysis of oxidative stability of polymers*, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 9-14, Orlando, Florida, **2003**; Paper 280-7.

Potyrailo, R. A.; Morris, W. G. *High-throughput development of new sensor materials using multichannel acoustic-wave sensor system,* Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 9-14, Orlando, Florida, **2003**; Paper 470-5.

Wroczynski, R. J.; Potyrailo, R. A.; Rubinsztajn, M.. *High Throughput Methods for Evaluation of Process Degradation of Polymer Formulations*, ANTEC **2003**---Proceedings of the 61st Annual Technical Conference & Exhibition, Vol. XLIX, Nashville, TN, May 4---8. Society of Plastics Engineers, pp. 2679-2683.

Potyrailo, R. A. *Combinatorial and High-throughput Experimentation for Development of Sensor Materials: New Scientific Method or Edisonian Approach Revisited?*, Institute for Instrumental Analysis, May 7, Karlsruhe, Germany, **2003**.

Potyrailo, R. A. *Combinatorial Development and Accelerated Performance Testing of Polymers*, 2nd DPI workshop on Combinatorial Material Research, May 15-16, Eindhoven, The Netherlands, **2003**.

Potyrailo, R. A.; Wroczynski, R. J.; Morris, W. G.; Bradtke, G. R., *Determination of Oxidative Stability of Polypropylene Using Chemical Sensors*, Polym. Degrad. Stab., accepted for publication July 17, **2003**.

References

1. Breyfogle, F. W. *Implementing Six Sigma*, 240-255, Wiley, New York (1999).
2. Potyrailo, R. A. Combinatorial Screening, In *Encyclopedia of Materials: Science and Technology*; K. H. J. Buschow; R. W. Cahn; M. C. Flemings; B. Ilschner; E. J. Kramer and S. Mahajan, Eds.; Elsevier: Amsterdam, The Netherlands, 2001; Vol. 2; 1329-1343.
3. Potyrailo, R. A. *Analytical Infrastructure for High Throughput Characterization of Combinatorial Materials Libraries*, Presented at COMBI 2002 - The 4th Annual International Symposium on Combinatorial Approaches for New Materials Discovery, January 23 - 25, San Diego, CA, 2002.
4. Potyrailo, R. A.; May, R. J. Rev. Sci. Instrum. **2002**, *73*, 1277-1283.
5. Potyrailo, R. A. Proc. SPIE-Int. Soc. Opt. Eng. **2002**, *4578* (Fiber Optic Sensor Technology and Applications 2001), 366-377.
6. Allen, N. S.; Homer, J.; McKellar, J. F. Chem. Ind. (London) **1976**, *16*, 692-693.
7. Allen, N. S.; Cundall, R. B.; Jones, M. W.; McKellar, J. F. Chem. Ind. (London) **1976**, *3*, 110-111.
8. Jacques, P. P. L.; Poller, R. C. Eur. Polym. J. **1993**, *29*, 75-81.
9. Jacques, P. P. L.; Poller, R. C. Eur. Polym. J. 1993, 29, 83-89.
10. Nelson, B. I. Proc. NATAS Ann Conf, 28, 617 (2000).
11. Schwarzenback, K., et. al., 24-30, *Plastics Additives Handbook*; Zweifel, H., Ed.; Hanser: Munich, Germany, 2001.
12. DACA Instruments, MicroCompounder Operation Manual, Rev 9/00-1.0, pp. 29-31, (2000).
13. Bagley, E.B.; Duffey, H. J. Trans. Soc. Rheol., 14, 545 (1970).
14. Yamane, H.; White, J. L. Polym. Eng. Sci., 23, 516 (1983).
15. Maxwell, B.; Nguyen, M. Soc. Plast. Eng., Tech. Pap. (1978), 24, 540 (1978).
16. Maxwell, B. Plast. Eng., 43, 41 (1987).
17. Matisova-Rychla, L.; Rychly, J. In *Degradation, Stabilization, and Lifetime Prediction*; R. L. Clough; N. C. Billingham and K. T. Gillen, Eds.; Advances in Chemistry Series 249; American Chemical Society: Washington, DC, 1996; 249; 175-193.
18. Kohler, D. R.; Krohnke, C. Polym. Degrad. Stab. **1998**, *62*, 385-393.
19. Patel, S. H.; Xanthos, M. Adv. Polym. Techn. **2001**, *20*, 22-41.
20. *Thermoplastic Polymer Additives. Theory and Practice*; Lutz, J. T., Jr., Ed.; Marcel Dekker: New York, NY, 1989.
21. *Plastics Additives Handbook*; Zweifel, H., Ed.; Hanser: Munich, Germany, 2001.
22. Handbook of Biosensors and Electronic Noses. Medicine, Food, and the Environment; Kress-Rogers, E., Ed.; CRC Press: Boca Raton, 1997.
23. Albert, K. J.; Lewis, N. S.; Schauer, C. L.; Sotzing, G. A.; Stitzel, S. E.; Vaid, T. P.; Walt, D. R. Chem. Rev. **2000**, *1000*, 2595-2626.
24. *Sensors Update*; Baltes, H.; Göpel, W.; Hesse, J., Eds.; VCH: Weinheim, 1996.
25. Thompson, M.; Stone, D. C. Surface-Launched Acoustic Wave Sensors: Chemical Sensing and Thin-Film Characterization; Wiley: New York, NY, 1997, p 196.

26. Ballantine, D. S., Jr.; White, R. M.; Martin, S. J.; Ricco, A. J.; Frye, G. C.; Zellers, E. T.; Wohltjen, *H. Acoustic Wave Sensors: Theory, Design, and Physico-Chemical Applications*; Academic Press: San Diego, CA, 1997, p 436.

27. Potyrailo, R. A.; Hobbs, S. E.; Hieftje, G. M. Fresenius' J. Anal. Chem. **1998**, *362*, 349-373.

28. Hierlemann, A.; Schweizer-Berberich, M.; Weimar, U.; Kraus, G.; Pfau, A.; Göpel, W., Pattern recognition and multicomponent analysis, In *Sensors Update*, Vol. 2; H. Baltes; W. Göpel and J. Hesse, Eds.; VCH: Weinheim, 1996; 119-180.

29. Gardner, J. W.; Hines, E. L., In Pattern analysis techniques, In Handbook of Biosensors and Electronic Noses. Medicine, Food, and the Environment; E. Kress-Rogers, Ed.; CRC Press: Boca Raton, FL, 1997; 633-652.

30. Potyrailo, R. A.; Wroczynski, R. J.; Morris, W. G.; Bradtke, G. R. Determination of oxidative stability of polymers using chemical sensors, In *Abstracts of 9th International Meeting on Chemical Sensors*, Boston, MA, July 2002, Elsevier Science: 2002; 300.

31. Potyrailo, R. A.; Sivavec, T. M.; Bracco, A. A. Proc. SPIE-Int. Soc. Opt. Eng. **1999**, *3856* (Internal Standardization and Calibration Architectures for Chemical Sensors), 140-147.

32. Potyrailo, R. A.; Sivavec, T. M., New polymer materials for environmental chemical sensors, In *Abstracts of 9th International Meeting on Chemical Sensors*, Boston, MA, July 2002 Elsevier Science: 2002; 119.

33. Beebe, K. R.; Pell, R. J.; Seasholtz, M. B. *Chemometrics: A Practical Guide*; Wiley: New York, NY, 1998.

34. Otto, M. Chemometrics: Statistics and Computer Application in Analytical Chemistry; Wiley-VCH: Weinheim, Germany, 1999.

35. Wise, B. M.; Kowalski, B. R., Process Chemometrics, In *Process Analytical Chemistry*; F. McLennan and B. Kowalski, Eds.; Chapman & Hall: London, England, 1995; 259-312.

36. Wroczynski, R. J.; Potyrailo, R. A.; Rubinsztajn, M.; Enlow, W. P. Micro-scale extrusion for the accelerated development of new polymeric materials, In *ANTEC 2002 - Annual Technical Conference,* May 2002, San Francisco, CA, Society of Plastic Engineers, Inc.: Brookfield, CT, 2002; Vol. 60; paper 693.

37. Guilbault, G. G., Applications of quartz crystal microbalances in analytical chemistry, In *Applications of Piezoelectric Quartz Crystal Microbalances*; C. Lu and A. W. Czanderna, Eds.; Elsevier: Amsterdam, The Netherlands, 1984; 251-280.

38. Ingle, J. D., Jr.; Crouch, S. R. *Spectrochemical Analysis*; Prentice Hall: Englewood Cliffs, NJ, 1988.

39. Blacker, R. S.; Birley, A. W. Polymer Testing **1991,** *10*,241.

40. Littman, A. M.; Fowler, N. E. Polym. Plast. Technol. Eng. **1982**,*18,* 93.

41. Baumgartner, G., Electrostatic Decay Measurement. Theory and Applications. EOS/ESD Symposium **1995**, 95-262.

42. Jonassen, N. *How Fast Does a Charge Decay?*, www.ce-mag.com.

43. LeGrand, D. G.; et. al. *Electrostatic Charging of Injection Molded Thermoplastics* **1996**, *96CRD180*, GE Research and Development Technical Report.

44. Knight, C. C.; McCloskey, P.; Shanklin, E. *Reduction of Static Charge on Compact Discs Molded from Melt OQ Resin* **1998**, *98CRD023*, GE Research and Development Technical Report.

45. Shishido Electrostatic Ltd, Operation Manual, *Static Honestmeter #H-0110*, Japan.

46. Haward, R.N. Trans. Faraday Soc. **1943**, *39,* 267.

47. Marshall, T.; Thompson, A.B. Proc. Royal Soc. A **1954**, *22,1* 541.

48. Rittel, D. Fracture of Polymers, Composites and Adhesives **2000**, *27,* 375.

49. Favro, L. D.; Wang, Yingxia; Telenkov, S. A.; Han, Xiaoyan; Kuo, P. K.; Thomas, R. L. Proc. Annu. Meet. Adhes. Soc. **1998**, *21*, 209.

50. Lindhagen, J. E.; Berglund L. A., J. Mater. Sci. **1997**, *32*(15), 4071.

51. Meredith C.; Sormana J.L; Tona A.; Elgendy H.; Karim A. Amis, E., ACS Polymer Preprints **2001**, *42*(2), 650.

52. Pharr, G.M. Materials Sci Eng. **1998**, *A253*, 151.

53. Asif, S.A.; Syed, Wahl, K.J.; Colton, R.J. Rev Sci Instrum. **1999**, *70*(5), 2408.

54. McColm, I.J. *Ceramic Hardness*, Plenum Press, New York, 1990; pp. 238-239.

55. Ferry, J.D. *Viscoelastic Properties of Polymers*; Wiley & Sons: New York, 1961.

56. Gendron, R.; Dumoulin, M. M.; Piche, L. Polym. Mater. Sci. Eng. **1995**, *72*, 23.

57. Gendron, R.; Piché, L.; Hamel, A.; Dumoulin, M.M.; Tatibouët, J. SPE ANTEC Tech Papers. **1997**, *43*, 334.

58. Gendron, R.; Dumoulin, M.M.; Piché, L.; Tatibouët, J.; Hamel, A. SPE ANTEC Tech. Papers. **1993**, *39*, 2256.

59. Gendron, R.; Tatibouët, J.; Guévremont, J.; Dumoulin, M.M.; Piché, L. Poly. Eng. Sci. **1995**, *35*, 79.

60. Gendron, R.; Dumoulin, M.M.; Tatibouët, J.; Piché, L. Proc. Polym. Processing Society 9th Annual Meeting 1993; 165.

61. Gendron, R.; Daigneault, L.E.; Tatibouët, J.; Dumoulin, M.M. Adv. Polym. Technol. **1996**, *15*(2), 111.

62. Abdellah, A. SPE ANTEC Tech Papers **2000**, *58*(1), 352.

63. Potyrailo, R. A. Stability enhancement of quartz crystal microbalance chemical sensors, Six Sigma Final Report Out, GE CRD, Schenectady, NY, October 6, 1998.

64. Mark, H.; Workman, J. *Statistics in Spectroscopy*; Academic Press: San Diego, CA, 1991.

65. Campbell, C. K. Surface Acoustic Wave Devices for Mobile and Wireless Communications; Academic Press: San Diego, CA, 1998.

66. Potyrailo, R. A.; Wroczynski, R. J.; Lemmon, J. P.; Flanagan, W. P.; Siclovan, O. P., J. Comb. Chem. **2003**, *5*, 8.

67. Potyrailo, R. A., Trends Anal. Chem. **2003**, *22*, 374-384.

68. Al-Malaika, S.; Goodwin, C.; Issenhuth, S.; Burdick D. Poly. Degr. Stab. 1999, 64, 145.

69. Fearon, P.K.; Marshall, N.; Billingham, N.C.; Bigger, S. W. J. Appl. Poly. Sci. **2001**, *79*, 733.

70. O'Driscoll, A. J.; Kramer, E.; Gupta, A. Int. Conf. Addit. Polyolefins **1998**, 293.

71. Dayal, U.; Mathur, A. B.; Dixit, S. Polym. Sci. **1994**, *2*, 899.

72. Stein, D.; Stevenson, D. SPE ANTEC Techn. Papers. **1999**, *57(2)*, 2276.
73. Gardner, P.; Gray, C.; Simmons, L. Polyolefins X, Int. Conf. **1997**, 615.
74. Dietz, S.; ACS Symp. Ser. **1992**, *513*, 134.
75. Ashton, H. C.; TAPPI Polym. Laminations Coat. Conf. **1999**, *1*, 401.
76. Hozner, A.; Chmil, K. In Plastics Additives Handbook; Zweifel, H., Ed.; Hanser: Munich, Germany, **2001**, 496-509.
77. Thompson, M.; Puaux, J. P.; Hrymak, A. N.; Hamielec A. E. Intern. Polymer Processing X **1995**, *2*, 111.
78. Hu, G-H, Kadri I. Polym. Eng. Sci. **1999**, *39*(5), 930.
79. Unlu, E.; Faller, J. F. Polym. Eng. Sci. **2001**, *41*(5), 743.
80. Kao, S. V.; Allison, G. R. Polym. Eng. Sci. **1984**, *24*(9), 645.
81. Gao, J.; Walsh, G. C.; Bigio, D., Briber; R. M., Wetzel, M. D. AIChe J., **45**(12) 2541 (1999).
82. Potyrailo, R. A., Wroczynski, R. J., Pickett, J. A., Rubinsztajn, M. Macromol. Rapid. Commun., **2003**, *24*, 123-130.

ATTACHMENTS

NEEDS MAPPING DOCUMENT

COMBINATORIAL MICROCOMPOUNDING/HIGH-THROUGHPUT

SCREENING PRODUCT DEVELOPMENT PLATFORM

K-TRON INTERNATIONAL, INC.
ROUTES 55 & 553
PITMAN, NJ 08071

VISION

A fully integrated product development platform incorporating a microcompounder directly linked to on-line (and where necessary off-line) microanalysis instrumentation. A common control system will provide recipe control and sequencing, process control, microanalytical instrumentation control, data processing, combinatorial library management and communication with the customer's laboratory management systems. Initial offering will address needs of polymer/additive formulations focused on polymer stabilization. Subsequent versions will be fully capable of polymer compounding and reactive extrusion processing. The system is envisioned to be tabletop size and compatible with the materials development laboratory environment.

First we would like to identify who you are and with whom we are having these discussions. Also (and this is optional on your part) we would like to understand a bit about your product development environment.

THE CUSTOMER

Your Company _____

Location   _____

Contact(s):   <u>Name</u>   <u>Phone</u>   <u>e-Mail</u>

(1)   _____   _____   _____

(2)   _____   _____   _____

(3)   _____   _____   _____

1

CURRENT DEVELOPMENT ENVIRONMENT (This Section Optional)

Lab Scale Compounding	Yes ☐	No ☐	
Single Screw	Yes ☐	No ☐	Size(s) _____
Kneader	Yes ☐	No ☐	Size(s) _____
Twin Screw			
Co Rotating	Yes ☐	No ☐	Size(s) _____
Counter Rotating	Yes ☐	No ☐	Size(s) _____

Lab Scale Feeders	Yes ☐	No ☐	
Volumetric Screw	Yes ☐	No ☐	Size(s) _____
Gravimetric Screw	Yes ☐	No ☐	Size(s) _____
Vibratory	Yes ☐	No ☐	Size(s) _____
Belt	Yes ☐	No ☐	Size(s) _____
Other	Yes ☐	No ☐	Specify _____

Typical Operation
     Extrusion Rate   _____
     Batch Size   _____
     Batches/Day   _____
     Number Feeders/Line   _____
     Min Feeder Rate   _____
     Max Feeder Rate   _____

PROPERTIES USED TO PROFILE PERFORMANCE

(1) _____   How Measured _____
(2) _____   How Measured _____
(3) _____   How Measured _____
(4) _____   How Measured _____
(5) _____   How Measured _____

CUSTOMER NEEDS

Now, please think about an alternative to your current practice that would be based on a microcompounding/high throughput screening product development paradigm. What would such a system need to look like to make it an attractive alternative to your current mode of operation?

- The Microcompounder Line
    Compounder Rate . . . Min _____ Max _____
    Type . . .   SSE _____ TSE _____ Kneader _____
    If TSE . . .   Co _____ Counter _____

If TSE . . . Segmented Screws   Yes ☐   No ☐
Split Barrel Capability   Yes ☐   No ☐

Other _____

Feeders . . . Number Per Line _____

Rate   (#1) _____ Min   _____ Max
        (#2) _____ Min   _____ Max
        (#3) _____ Min   _____ Max
        (#4) _____ Min   _____ Max

Type: SS _____   TS _____   VIBR _____   Other _____

Feed Stocks: Powder   Yes ☐   No ☐   Ex _____
              Flake   Yes ☐   No ☐   Ex _____
              Pellet   Yes ☐   No ☐   Ex _____

Other _____

- Controls/Systems Integration
  Do you need to integrate this system into a laboratory automation/management system?   ☐ Yes ☐ No

  If Yes, what must it link to: _____

  Do you have preferences for data management, spreadsheet analyses or other software packages that would/could be incorporated into the system? Yes☐ No☐

  If Yes, what are they:_____

  _____

- Microanalysis (High Throughput Screening)
  List 5 polymer properties in rank order
   (Most Important = 1; Least Important = 5)

      (1) _____
      (2) _____
      (3) _____
      (4) _____
      (5) _____

Do these five properties sufficiently profile performance?   Yes ☐   No ☐

If Not, how many are needed? _____

What are they?   _____
                      _____
                      _____

Please rank on-line (real time) microanalysis and off-line (rapid) microanalysis:

On-line (1 or 2) _____

Off-line (1 or 2) _____

Let's explore how a microcompounding/high throughput screening product development system would best meet your needs from a strategic as well functional perspectives.

Would increased productivity (as measured by samples/results per day) of your material development activities be of value? Yes ☐   No ☐

If Yes . . . what faction of improvement would be an incentive to adopt an alternative. . .

   2X ☐   5X ☐   10X ☐   Other _____

If No . . . . Why?
_____
_____
_____
_____
_____
_____
_____
_____
_____

This envisioned system is targeted to allow one product developer to generate and evaluate samples at a rate of 10X that of their current operation. In addition, the material and energy consumed (on a per sample/result basis) is likely to be 10X less than that of the current operation.

- • Will such a productivity improvement justify an investment in such a capability?
  Yes ☐   No ☐

4

- Will the projected material and energy savings be important in your investment decision?

  Yes ☐   No ☐

- What are other technical considerations that enter the justification question?

Accuracy (absolute)	Yes ☐	No ☐
Accuracy (ranking)	Yes ☐	No ☐
System Reliability	Yes ☐	No ☐
System Expandability	Yes ☐	No ☐
System Adaptability	Yes ☐	No ☐
System Automation	Yes ☐	No ☐
Ability to Manually Operate	Yes ☐	No ☐
Ease of Use	Yes ☐	No ☐
Other	Yes ☐	No ☐

- What about size . . . what is ideal "foot print" _____

  What about Weight _____

  Emissions Control _____

  Area Classification _____

- How about cost of such a system . . . remember, it will be a fully integrated system including microcompounder, feeders, compounded melt management, microanalysis, controls and data/library management. On a cost per sample/result criteria, what do you think constitutes:

  "Buy it Today" _____

  "Put it in the Budget" _____

  "No Way – Too Expensive" _____

In Conclusion

(1) What would make a combinational microcompounding/high throughput screening product development platform a "Wow/Got to Have Capability"?

  _____
  _____
  _____
  _____
  _____

(2) What would potential showstoppers be?

  _____
  _____
  _____
  _____
  _____
  _____

(3) Other Comments? _____

_____

_____

September 5, 2002

Dear :

For more than ten years, the pharmaceutical industry has been quietly experiencing a revolution in product development. The one-at-a-time synthesis, testing and evaluation of new therapeutic substances are being replaced with a new development paradigm that dramatically quickens the pace of development activities. Commonly referred to as combinational chemistry/high throughput screening, it enables in a given period of time, an increase in the generation and assessment of experimental substances by orders of magnitude while at the same time consuming orders of magnitude less material. It's a fast, efficient and effective product development paradigm . . . and . . . is applicable to materials development.

Indeed, the materials technology community has been expressing growing levels of interest in combinational/high throughput screening methods. Active programs exist in the industrial, academic and governmental sectors. With respect to the development of polymer formulations, this new product development paradigm emerges as combinational microcompounding coupled with rapid microanalysis. Properly engineered, such a product development platform would enable the generation and assessment of polymer formulations with the advantages of speed, efficiency and effectiveness currently enjoyed by those using combinational methods in the pharma industry. It is bringing these advantages into your operation that I would like to discuss with you.

K-Tron International, in collaboration with General Electric Global Research and Cytec Industries, are engaged in a Department of Energy funded development of a suite of microanalysis techniques that can rapidly measure attributes of experimental product formulations being generated from a combinational microcompounding processor.

General Electric Global Technology is the primary contractor and has the responsibility for developing the enabling microanalytic hardware and methods. Cytec Industries has the responsibility for validating these methods. It is not the objective of either of these parties to commercialize the developed technology.

K-Tron International is the designated commercial development partner. As such, K-Tron has the responsibility for developing a commercial product design that effectively integrates combinational methods, microcompounding capability and rapid microanalytical techniques. But . . . to develop a rational set of specifications, K-Tron would like to engage you in a "needs mapping" discussion to better frame just what such combinational microcompounding/high throughput microanalysis product platform should look like to suit your product development needs. The initial effort is focused on the development process for relatively simple polymer/additive formulations. Future generations of this product platform will address the needs of polymer blends and reactive extrusion.

Please find as an attachment a discussion tool we have developed to guide us through the needs mapping exercise and to capture those features critical to the success of your product development efforts. The proposed discussion and the information ultimately captured is intended to develop a database for which the specifications of a combinatorial-microcompounding/high throughput microanalysis system can be developed It is *not* our intention to capture and publish sensitive or proprietary information.

I am asking you to review the discussion tool and consider engaging in this needs mapping process in the near future. I anticipate the process will take two to four hours to execute. It is probably best done in a small group setting with up to two representatives from K-Tron and a number of product development stakeholders from your enterprise.

I will give you a call in the next few days to further explore your interest in participating in this process. Alternatively, you can call (856-256-3258) or e-mail me (jgolba@ktron.com) beforehand.

Thank you for your consideration on this matter.

Sincerely,

Joseph C. Golba, Jr., PhD
Vice President, R&D

JG:jt

Enclosure

0014JG

NEEDS MAPPING DOCUMENT

COMBINATORIAL MICROCOMPOUNDING/HIGH-THROUGHPUT

SCREENING PRODUCT DEVELOPMENT PLATFORM

K-TRON INTERNATIONAL, INC.
ROUTES 55 & 553
PITMAN, NJ 08071

<u>**VISION**</u>

A fully integrated product development platform incorporating a microcompounder directly linked to on-line (and where necessary off-line) microanalysis instrumentation. A common control system will provide recipe control and sequencing, process control, microanalytical instrumentation control, data processing, combinatorial library management and communication with the customer's laboratory management systems. Initial offering will address needs of polymer/additive formulations focused on polymer stabilization. Subsequent versions will be fully capable of polymer compounding and reactive extrusion processing. The system is envisioned to be tabletop size and compatible with the materials development laboratory environment.

First we would like to identify who you are and with whom we are having these discussions. Also (and this is optional on your part) we would like to understand a bit about your product development environment.

<u>**THE CUSTOMER**</u>

Your Company INDUSTRIAL #1

Location

Contact(s):	<u>Name</u>	<u>Phone</u>	<u>e-Mail</u>
(1)			
(2)			
(3)			

<u>**CURRENT DEVELOPMENT ENVIRONMENT (This Section Optional)**</u>

Lab Scale Compounding	Yes ■	No ☐	
Single Screw	Yes ■	No ☐	Size(s) _____
Kneader	Yes ■	No ☐	Size(s) _____
Twin Screw			
Co Rotating	Yes ■	No ☐	Size(s) _____
Counter Rotating	Yes ■	No ☐	Size(s) _____

Lab Scale Feeders	Yes ■	No ☐	
Volumetric Screw	Yes ■	No ☐	Size(s) T-20, S-60
Gravimetric Screw	Yes ■	No ☐	Size(s) T-20, S-60, T-35
Vibratory	Yes ☐	No ☐	Size(s) _____
Belt	Yes ☐	No ☐	Size(s) _____
Other	Yes ■	No ☐	Specify _____

Typical Operation

Extrusion Rate	20 – 200 lb/hr
Batch Size	5 – 50 lb/hr
Batches/Day	20
Number Feeders/Line	2 - 4
Min Feeder Rate	20 mg/min
Max Feeder Rate	100 lb/hr

PROPERTIES USED TO PROFILE PERFORMANCE

1. Dispersion Quality   How Measured Visual Inspection/Microscopy
2. Viscosity   How Measured MFI, Rheology
3. Specific Gravity/Ash   How Measured Compositional Consistency
4. Physical Properties   How Measured Tensile, Elongation, Flexural
5. Color Matching   How Measured SPE

CUSTOMER NEEDS

Now, please think about an alternative to your current practice that would be based on a microcompounding/high throughput screening product development paradigm. What would such a system need to look like to make it an attractive alternative to your current mode of operation?

- The Microcompounder Line
  Compounder Rate . . . Min 2 lb/hr   Max 10 lb/hr
  Type . . .   SSE _____   TSE X   Kneader _____ If TSE
  . . .   Co X   Counter _____
     If TSE . . . Segmented Screws   Yes ☐   No ■

Split Barrel Capability   Yes ■   No □

    Other _____Upstream Size Reduction Equipment_____

Feeders . . . Number Per Line 1 or 2 _____

    Rate   (#1)   0.5 lb/hr Min   2 lb/hr Max
            (#2)   2 lb/hr Min   10 lb/hr Max
            (#3)   _____ Min   _____ Max
            (#4)   _____ Min   _____ Max

    Type: SS _X___   TS _X___   VIBR _____ Other Liquid Injection

    Feed Stocks: Powder   Yes ■   No □   Ex _____
                   Flake   Yes ■   No □   Ex _____
                   Pellet   Yes ■   No □   Ex _____

            Other _Liquid_____

- Controls/Systems Integration
  Do you need to integrate this system into a laboratory automation/management system?
          Yes■   No □

  If Yes, what must it link to: Product Development Database _____

  Do you have preferences for data management, spreadsheet analyses or other software
  packages that would/could be incorporated into the system? Yes■ No□

  If Yes, what are they:_Excel spreadsheet_____

  _____

- Microanalysis (High Throughput Screening)
  List 5 polymer properties in rank order
   (Most Important = 1; Least Important = 5)

      (1) _Viscosity_____
      (2) _Dispersion_____
      (3) _Compositional Analysis_____
      (4) Color Match/Dispersion (Δ Pressure)
      (5) _Chemical Analysis – XRF, IR, GCMS_____

Do these five properties sufficiently profile performance?　　Yes ■　　　　No ☐

If Not, how many are needed? _____

What are they?　　　　　_____
　　　　　　　　　　　　_____
　　　　　　　　　　　　_____

Please rank on-line (real time) microanalysis and off-line (rapid) microanalysis:

On-line (1 or 2) Viscosity/Dispersion/Color Match

Off-line (1 or 2) Chemical Analysis

Let's explore how a microcompounding/high throughput screening product development system would best meet your needs from a strategic as well functional perspectives.

Would increased productivity (as measured by samples/results per day) of your material development activities be of value? Yes　■　　　No　☐

If Yes . . . what faction of improvement would be an incentive to adopt an alternative. . .

　　2X ☐　　　　5X ■　　　　10X ☐　　　　Other minimum 5X; preferable 10X with less
　　　　　　　　　　　　　　　　　　　　　　　　　　material

If No . . . . Why?

_____
_____
_____
_____
_____
_____
_____
_____
_____
_____

This envisioned system is targeted to allow one product developer to generate and evaluate samples at a rate of 10X that of their current operation. In addition, the material and energy consumed (on a per sample/result basis) is likely to be 10X less than that of the current operation.

- Will such a productivity improvement justify an investment in such a capability?
  Yes　■　　　No　☐

- Will the projected material and energy savings be important in your investment decision?
  Yes ☐   No ■

- What are other technical considerations that enter the justification question?
Accuracy (absolute)	Yes ■	No ☐
Accuracy (ranking)	Yes ■	No ☐
System Reliability	Yes ■	No ☐
System Expandability	Yes ■	No ☐
System Adaptability	Yes ■	No ☐
System Automation	Yes ■	No ☐
Ability to Manually Operate	Yes ■	No ☐
Ease of Use	Yes ■	No ☐
Other	Yes ☐	No ☐

- What about size . . . what is ideal "foot print" <u>Table-top (~4' x 3')</u>
  What about Weight _____
  Emissions Control _____
  Area Classification _____

- How about cost of such a system . . . remember, it will be a fully integrated system including microcompounder, feeders, compounded melt management, microanalysis, controls and data/library management. On a cost per sample/result criteria, what do you think constitutes:

  "Buy it Today" <u>$85,000 total cost</u>
  "Put it in the Budget" <u>$150,000</u>
  "No Way – Too Expensive" <u>$200,000</u>

In Conclusion

(1) What would make a combinational microcompounding/high throughput screening product development platform a "Wow/Got to Have Capability"?

   <u>Reasonable cost, maximum process flexibility, capability to feed standard</u>
   <u>pellet geometry, good scaling to/from Coperion equipment, sized equivalent</u>
   <u>to Brabender</u>

(2) What would potential showstoppers be?
   <u>Cost, limitations to feed intake of standard materials not able to duplicate on</u>
   <u>Popular co-rotating twin screw models.</u>

(3) Other Comments? _____

_____

_____

NEEDS MAPPING DOCUMENT

COMBINATORIAL MICROCOMPOUNDING/HIGH-THROUGHPUT

SCREENING PRODUCT DEVELOPMENT PLATFORM

K-TRON INTERNATIONAL, INC.
ROUTES 55 & 553
PITMAN, NJ 08071

VISION

A fully integrated product development platform incorporating a microcompounder directly linked to on-line (and where necessary off-line) microanalysis instrumentation. A common control system will provide recipe control and sequencing, process control, microanalytical instrumentation control, data processing, combinatorial library management and communication with the customer's laboratory management systems. Initial offering will address needs of polymer/additive formulations focused on polymer stabilization. Subsequent versions will be fully capable of polymer compounding and reactive extrusion processing. The system is envisioned to be tabletop size and compatible with the materials development laboratory environment.

First we would like to identify who you are and with whom we are having these discussions. Also (and this is optional on your part) we would like to understand a bit about your product development environment.

THE CUSTOMER

Your Company INDUSTRIAL #2 _____

Location   _____

Contact(s):   <u>Name</u>   <u>Phone</u>   <u>e-Mail</u>

(1)   _____   _____   _____

(2)   _____   _____   _____

(3)   _____   _____   _____

CURRENT DEVELOPMENT ENVIRONMENT (This Section Optional)

Lab Scale Compounding	Yes ■	No ☐	
Single Screw	Yes ■	No ☐	Size(s) ¾"; 1"
Kneader	Yes ☐	No ☐	Size(s)
Twin Screw			
Co Rotating	Yes ■	No ☐	Size(s) 30 mm
Counter Rotating	Yes ■	No ☐	Size(s) 34 mm

Lab Scale Feeders	Yes ■	No ☐	
Volumetric Screw	Yes ■	No ☐	Size(s) 1 – 50#/hr
Gravimetric Screw	Yes ■	No ■	Size(s) 1 – 50#/hr
Vibratory	Yes ☐	No ■	Size(s)
Belt	Yes ☐	No ☐	Size(s)
Other	Yes ☐	No ☐	Specify

Typical Operation
- Extrusion Rate   1 to 30 lb/hr
- Batch Size   5 to 25 lb/hr
- Batches/Day   1 to 10 lb/hr
- Number Feeders/Line   2
- Min Feeder Rate   1 lb/hr
- Max Feeder Rate   50 lb/hr

PROPERTIES USED TO PROFILE PERFORMANCE

1. Moderlus vs. Temp   How Measured DMA
2. Viscosity vs. Temp/Shear Rate   How Measured Capillary;Parallel Plate Rheometer
3. Tensile Properties   How Measured Instrum
4. Impact Properties   How Measured Izod & Dynastup
5. Color   How Measured Spectrophotometer
6. Film Characteristics

CUSTOMER NEEDS

Now, please think about an alternative to your current practice that would be based on a microcompounding/high throughput screening product development paradigm. What would such a system need to look like to make it an attractive alternative to your current mode of operation?

- The Microcompounder Line
  - Compounder Rate . . .   Min 1/2   Max 5 lb/hr

Type . . .   SSE X_____   TSE ____X__   Kneader _____
If TSE . . .   Co X_____   Counter _____
    If TSE . . . Segmented Screws   Yes ■   No ☐
    Split Barrel Capability   Yes ■   No ☐

Other _____

Feeders . . . Number Per Line 2-3, including liquid addition _____

Rate   (#1) _____ Min   _____ Max
      (#2) _____ Min   _____ Max
      (#3) _____ Min   _____ Max
      (#4) _____ Min   _____ Max

Type: SS _____   TS _____   VIBR _____   Other _____

Feed Stocks: Powder   Yes ■   No ☐   Ex _____
              Flake   Yes ■   No ☐   Ex _____
              Pellet   Yes ■   No ☐   Ex _____

Other _Liquid_____

- Controls/Systems Integration
  Do you need to integrate this system into a laboratory automation/management
  system?   ☐ Yes ■ No

  If Yes, what must it link to: _____

  Do you have preferences for data management, spreadsheet analyses or other
  software packages that would/could be incorporated into the system? Yes☐ No☐

  If Yes, what are they:_____

  _____

- Microanalysis (High Throughput Screening)
  List 5 polymer properties in rank order
  (Most Important = 1; Least Important = 5)

  (1)   Thermal properties – DSC, DMA, TGA
  (2)   Rheological properties
  (3)   Physical properties – tensile, flexural strength, impact
  (4)   Color
  (5)   Flammability, weatherability, etc.

Do these five properties sufficiently profile performance?   Yes ■   No ☐

If Not, how many are needed? _____

What are they?   _____
                      _____
                      _____

Please rank on-line (real time) microanalysis and off-line (rapid) microanalysis:

On-line (1 or 2) <u>Composition & Visco-Elastic Properties</u>

Off-line (1 or 2) <u>DSC, DMA & Physical Properties</u>

Let's explore how a microcompounding/high throughput screening product development system would best meet your needs from a strategic as well functional perspectives.

Would increased productivity (as measured by samples/results per day) of your material development activities be of value? Yes ■   No ☐

If Yes . . . what faction of improvement would be an incentive to adopt an alternative. . .

   2X ☐   5X ☐   10X ■++   Other _____

If No . . . . Why?
_____
_____
_____
_____
_____
_____
_____
_____
_____

This envisioned system is targeted to allow one product developer to generate and evaluate samples at a rate of 10X that of their current operation. In addition, the material and energy consumed (on a per sample/result basis) is likely to be 10X less than that of the current operation.

- Will such a productivity improvement justify an investment in such a capability?
  Yes ☐   No ■ Not at the present time!

- Will the projected material and energy savings be important in your investment decision?
  Yes ■   No ☐

- What are other technical considerations that enter the justification question?

Accuracy (absolute)	Yes ■	No ☐
Accuracy (ranking)	Yes ■	No ☐
System Reliability	Yes ■	No ☐
System Expandability	Yes ☐	No ■
System Adaptability	Yes ■	No ☐
System Automation	Yes ■	No ☐
Ability to Manually Operate	Yes ■	No ☐
Ease of Use	Yes ■	No ☐
Other	Yes ☐	No ☐

- What about size . . . what is ideal "foot print"
  What about Weight
  Emissions Control
  Area Classification

  > Not a big issue – less than current equipment!

- How about cost of such a system . . . remember, it will be a fully integrated system including microcompounder, feeders, compounded melt management, microanalysis, controls and data/library management. On a cost per sample/result criteria, what do you think constitutes:

  "Buy it Today"
  "Put it in the Budget"
  "No Way – Too Expensive"

  > Way too early to give adequate answer. Design it! Build it! And demonstrate its effectiveness.

In Conclusion

(1) What would make a combinational microcompounding/high throughput screening product development platform a "Wow/Got to Have Capability"?

   10 – 25X productivity improvement. Complete customization of compounding with many of the properties measured automatically.

(2) What would potential showstoppers be?
   Coupling between compounding & molding & testing.
   Customization
   Lack of on-line compositional analysis
   High Cost/Complexity/Set-up Time

5

(3) Other Comments? <u>The keys to a successful microcompounding technology are: 1) greatly improved productivity; 2) outstanding accuracy; 3) reliable translation of automated measurements to current offline test methodologies.</u>

NEEDS MAPPING DOCUMENT

COMBINATORIAL MICROCOMPOUNDING/HIGH-THROUGHPUT

SCREENING PRODUCT DEVELOPMENT PLATFORM

K-TRON INTERNATIONAL, INC.
ROUTES 55 & 553
PITMAN, NJ 08071

VISION

A fully integrated product development platform incorporating a microcompounder directly linked to on-line (and where necessary off-line) microanalysis instrumentation. A common control system will provide recipe control and sequencing, process control, microanalytical instrumentation control, data processing, combinatorial library management and communication with the customer's laboratory management systems. Initial offering will address needs of polymer/additive formulations focused on polymer stabilization. Subsequent versions will be fully capable of polymer compounding and reactive extrusion processing. The system is envisioned to be tabletop size and compatible with the materials development laboratory environment.

First we would like to identify who you are and with whom we are having these discussions. Also (and this is optional on your part) we would like to understand a bit about your product development environment.

THE CUSTOMER

Your Company ACADEMIC

Location

Contact(s):	Name	Phone	e-Mail
(1)			
(2)			
(3)			

CURRENT DEVELOPMENT ENVIRONMENT (This Section Optional)

Lab Scale Compounding	Yes ■	No □	
Single Screw	Yes ■	No □	Size(s) __1 ¼" Segmented__
Kneader	Yes □	No ■	Size(s) ————————
Twin Screw			
Co Rotating	Yes ■	No □	Size(s) __15mm, 30mm, 34 mm__
Counter Rotating	Yes ■	No □	Size(s) 20mm (WE),
			34 mm(L)

Lab Scale Feeders	Yes ■	No □	
Volumetric Screw	Yes ■	No □	__Size(s) S-200, T20, T35__
			Accurate
Gravimetric Screw	Yes ■	No □	Size(s) Acrison
Vibratory	Yes □	No ■	Size(s) _____
Belt	Yes □	No ■	Size(s) _____
Other	Yes □	No □	Specify _____

Typical Operation

Extrusion Rate	__1 – 50 lb/hr__
Batch Size	__1 – 50 lb/hr__
Batches/Day	__4 – 5, perhaps 6 (max)__
Number Feeders/Line	__2 main hopper; additional 1__ downstream
Min Feeder Rate	__1 lb/hr__
Max Feeder Rate	__50 lb/hr__

PROPERTIES USED TO PROFILE PERFORMANCE

1. __MFI__   How Measured Off line
2. __Tensile Properties__   How Measured "
3. __Impact Properties__   How Measured "
4. __Melt Strength__   How Measured "
5. __DSC__   How Measured "
6. Dispersed phase size   How Measured Optional

CUSTOMER NEEDS

Now, please think about an alternative to your current practice that would be based on a microcompounding/high throughput screening product development paradigm. What would such a system need to look like to make it an attractive alternative to your current mode of operation?

- The Microcompounder Line
  - Compounder Rate . . .   Min __Technically Limiting__   Max 1 lb/hr _____
  - Type . . .   SSE _____   TSE __X__   Kneader _____
  - If TSE . . .   Co __X__   Counter __X (for stuff like PVC)__

If TSE . . . Segmented Screws   Yes ■   No ☐
Split Barrel Capability   Yes ■   No ☐

Other <u>consider solid/segmented screw hybrid; L/D 20 to 24; downstream vent and feed ports</u>

Feeders . . . Number Per Line   <u>2 for solids</u>

Rate	(#1)	——— Min	<u>0.9 lb/hr</u>	Max
	(#2)	——— Min	<u>0.1 lb/hr</u>	Max
	(#3)	——— Min	——— Max	
	(#4)	——— Min	——— Max	

Type: SS ———   TS <u>X</u>   VIBR ———   Other ———

Feed Stocks: Powder   Yes ■   No ☐   Ex ———
               Flake   Yes ■   No ☐   Ex ———
               Pellet   Yes ■   No ☐   Ex ———

Other   <u>provide grinder (to reduce particle size)</u>

- Controls/Systems Integration
  Do you need to integrate this system into a laboratory automation/management system?
  Yes ■   No ☐

  If Yes, what must it link to: <u>provide a network connection (Ethernet link to customer tools)</u>

  Do you have preferences for data management, spreadsheet analyses or other software packages that would/could be incorporated into the system? Yes ■   No ☐

  If Yes, what are they: <u>Excel preferred</u>

  _____

- Microanalysis (High Throughput Screening)
  List 5 polymer properties in rank order
  (Most Important = 1; Least Important = 5)

  (1) <u>rheological parameters</u>
  (2) <u>mechanical properties</u>
  (3) <u>electrical properties (static)</u>
  (4) <u>color</u>
  (5) <u>die swell . . . elastic properties of resin</u>

3

Do these five properties sufficiently profile performance?   Yes ■   No ☐

If Not, how many are needed? _____

What are they?   _____
                      _____
                      _____

Please rank on-line (real time) microanalysis and off-line (rapid) microanalysis:

On-line (1 or 2) <u>viscosity, elasticity, color</u>

Off-line (1 or 2) <u>mech/elec.</u>

Let's explore how a microcompounding/high throughput screening product development system would best meet your needs from a strategic as well functional perspectives.

Would increased productivity (as measured by samples/results per day) of your material development activities be of value? Yes ■   No ☐   Would be attractive to their customers

If Yes . . . what faction of improvement would be an incentive to adopt an alternative. . .

2X ■   5X ☐   10X ☐   Other _____

If No . . . . Why?
_____
_____
_____
_____
_____
_____
_____
_____
_____

This envisioned system is targeted to allow one product developer to generate and evaluate samples at a rate of 10X that of their current operation. In addition, the material and energy consumed (on a per sample/result basis) is likely to be 10X less than that of the current operation.

- Will such a productivity improvement justify an investment in such a capability?
  Yes ■   No ☐

- Will the projected material and energy savings be important in your investment decision?
  Yes ■ mat'l   No ■ energy

- What are other technical considerations that enter the justification question?

Accuracy (absolute)	Yes ■	No ☐	be in range of eng. properties
Accuracy (ranking)	Yes ■	No ☐	
System Reliability	Yes ■	No ☐	
System Expandability	Yes ■	No ☐	modular
System Adaptability	Yes ■	No ☐	esp. control system
System Automation	Yes ■	No ☐	
Ability to Manually Operate	Yes ■	No ☐	
Ease of Use	Yes ■	No ☐	
Other	Yes ■	No ☐	

- What about size . . . what is ideal "foot print" <u>smaller is better ("hand carry" components)</u>
  What about Weight <u> lighter is better </u>
  Emissions Control <u> no – for customer to do </u>
  Area Classification <u> will depend on customer application; offer EX option </u>

- How about cost of such a system . . . remember, it will be a fully integrated system including microcompounder, feeders, compounded melt management, microanalysis, controls and data/library management. On a cost per sample/result criteria, what do you think constitutes:

  "Buy it Today" ——————————————
  "Put it in the Budget" ——————————————
  "No Way – Too Expensive" ——————————————

> This will be new/novel technology. . . may need to have loan/lease units for customer to evaluate

In Conclusion

(1) What would make a combinational microcompounding/high throughput screening product development platform a "Wow/Got to Have Capability"?

<u>Features to allow customer to optimize his process.</u>

(2) What would potential showstoppers be?
   <u>Poor Safety/Personnel Protection</u>
   <u>Difficult to work with</u>

(3) Other Comments? ——————————————
   ————————————————————
   ————————————————————

Attachment VI

Combinatorial Microcompounding
High Throughput Screening
Product Development Platform

Technical Specification

Distribution:

Project team & advisors:
KS:
KA:
KI: J. Foley, J. Golba
Colormax:

C:\Documents and Settings\wroczynski\My Documents\Additives\DOE Reports\Final Report\CCS_Spec.doc

Date / Issue (of Document)	1 July 15, 2003		2		3		4		5	
	Dept.	Inital	Dept.	Inital	Dept.	Inital	Dept.	Inital	Dept.	Inital
Issuer	KI R&D	JTF								
Approval	KI R&D									

	Ref:	Doc. No.:
K-TRON SODER	Total Bl/pg: 14 Bl/pg No: 1	**07.15. 00xx**

Form 20.23-0002 - 93-05

Combinatorial Compounding System	Design Specification

1 <u>General description of the product</u>

1.1 Project name

The K-Tron Soder name for this project is Combinatorial Microcompounding High Throughput Screening Product Development Platform. It may also be referred to as the Combinatorial Compounding System and may be abbreviated as CCS.

1.2 Development goals

The primary objective of this project is to develop an integrated bench-top polymer microcompounding system, which includes a suite of microanalysis instrumentation and techniques for rapid evaluation of polymer formulations, and incorporates a supervisory control system with a suitable interface to a laboratory data management system. The primary usage of the product is to enable the customer to accelerate the development of new polymer compounds using a combinatorial or high throughput experimentation methodology.

The system should be reliable, flexible, easy to use and easy to service. All equipment should be rugged enough for daily laboratory use. The compounding extruder and other material handling components should be easy to clean and provide for quick material changeover. The instrumentation components should be compact, stable and accurate, and be easy to test and calibrate. The user interface should be graphical in nature and simple to use by trained laboratory personnel. All components should be networked and accessible from the central user interface. The central controller should provide for fully automated unmanned operation of the system. The system components should be chosen and designed to be expandable and adaptable to future needs and updated technologies.

1.3 Project description

The project will have multiple phases based on the complexity of the polymer chemistry involved. The first phase will focus on Polymer/Additive Systems (Tier 1) and will define the basic platform for the later phases. The second phase will focus on Polymer/Polymer Systems (Tier 2) and the third phase will focus on Reactive Compounded Systems (Tier 3). The primary difference between the three tiers will be the configuration of the compounding system and the analysis techniques employed. This specification will focus primarily on the Tier 1 system. A unifying theme across the components of this infrastructure is a common platform for data acquisition, network communication between experimental stations, and data management systems.

The Tier 1 system focuses on additives since they are an essential and often expensive part of many polymer formulations. Additives play a crucial role in new materials development imparting enhanced or new performance properties. Suppliers are constantly seeking improvements in processing and higher output of finished products with an ever more sophisticated range of properties. However, current polymer test methods are slow, labor intensive, and require consumption of large quantities of test materials. As a result, the introduction of new additives technology is extremely slow and costly. The use of the Combinatorial Compounding System with rapid tests for polymer properties will enable a significant acceleration in the rate of new additives and plastics development opening up new materials applications through increased polymer performance, decreased cost of polymer development and manufacturing, and reduced energy consumption and waste production associated with disposal of poor performing or off-specification materials.

Each Combinatorial Compounding System will be comprised of three major sub-systems:
1. Microcompounder
2. Microanalysis instruments

3. User Interface and Control

The Microcompounder will consist of a co-rotating twin-screw extruder with its required drive section, electric heaters, and a local chiller for cooling. The extruder L/D as well as its screw configuration will be chosen based on the customer's specific requirements. The system will also require from two to four gravimetric microfeeders. The feeders will be chosen based on the required feed rates as well as the characteristics of the material to be fed. Typically, at the low rates required, an automatic refill system will not be necessary and feeders would be filled by hand. Small venturi style vacuum loaders will be offered as an option. It should also be possible to incorporate liquid ingredient feeders into the system. If necessary for the application, the extruder will feed a melt pump with it's own drive section which will be slaved to the drive of the extruder via the central control system. The output of the extruder (or melt pump) will be fitted with either a slit die or strand die as standard equipment. Die selection may be dependant on the types of on-line or post analysis, which are required. As the material exits the extruder, it may need to be cooled in a recirculating water bath. The final product will have to be automatically collected and prepared for any off-line analysis. This will require that the samples be marked by some permanent means so that they may be later identified.

The Microanalysis system will be configured based on customer and product requirements. It will consist of both on-line and off-line instrumentation. The on-line instrumentation will be mounted either directly in the melt stream or at the exit of the die. In general, the on-line instrumentation will be used to measure rheological properties, chemical composition, degradation byproducts, and color. The on-line instrumentation selection will consist of a rheometer, various spectroscopic sensors (UV, Visible, NIR, MIR), and an "electronic nose". In addition, more common measurements at the extruder will also be recorded, such as die and other zone pressures and temperatures, and screw torque. The off-line instrumentation will either be mounted after the material cooling bath and prior to the sample collection system or separate from the compounding system entirely if the sample requires additional preparation. The off-line instrumentation will primarily be used for the measurement of mechanical properties. They will provide nondestructive measurements, allowing multiple analyses to be made on the same library of samples. The off-line instruments employed will be unique in that they will generally use samples, which are much smaller than typical commercial equipment. The off-line instrumentation selection will consist of a mini biaxial impact tester, micro indentation tester, static charge dissipation tester, and other commercially available instruments as required. In many cases, the microanalysis instruments will not produce absolute measurements of the material property but will provide data, which correlates to the rank order of the property of interest. In other instances, multiple sensor data will be analyzed using more sophisticated multivariate analysis techniques in order to extract the require measurements.

The user interface and central control will primarily be PC based using a commercially available visualization software package. Individual components and sensors may utilize embedded controls and PLCs with integrated digital communication capabilities. The system interconnection will be based on a common protocol for data acquisition, network communication between experimental stations, and data management systems. The PC based operator interface will be the primary interface for all components of the system using a graphical representation of the device where possible. All setup and operational parameters will be available on the PC interface. In addition, the PC interface will have responsibility for central control and coordination of the system. The user interface will allow for manual control of all system components. However, the primary central control function is to execute a sequential recipe script, which defines material formulations as well as various machine parameters for the Microcompounding system. Formulation libraries can be generated by the use of existing combinatorial methods and/or design of experiments methods. The formulation directly determines the throughput of the material and additive feeders. The machine parameters in the recipe script would vary compounder variables such as screw/pump speed, zone temperatures, cooling temperature, etc. The central controller will also be responsible for collection of raw data from the Microanalysis system as well as control the sample collection and marking system. Analysis, organization, and archiving of the data and results will be handled externally in a separate networked laboratory data management system.

2 Market data

2.1 Position of the product in the line of products

The Combinatorial Compounding System will be an entirely new product in the product line.   It will, however, leverage our ability to design and control micro-feeding equipment as well as provide software for the overall control and management of compounding, analysis, and data management systems.

2.2 Replacement of existing products

It is not intended to directly replace any current products.

2.3 Exchangeability with other products

It is not intended to be directly exchangeable any current products.

2.4 Market introduction plan

The Combinatorial Compounding System will be available for field trials by _____ (as prototype version). Not all options will be available at this time. Full market introduction could be as early as _____, pending adequate BETA site availability, suitable for 6-month testing period.

2.5 Product life expectancy

The product commercial life has to be at least 10 years. With technology upgrades, the system concept could remain a viable product for up to 20 years.

2.6 Maximum manufacturing cost

Manufacturing cost is dependant on the system configuration as well as purchase quantities. Since system configuration is highly dependant on the instrumentation package, and those components represent a significant part of the cost, it is difficult at this time to accurately define a cost. A typical configuration for a Tier 1 application with extruder, three microfeeders, a basic instrumentation package (rheometer, near-IR, mid-IR, and UV spectrometer), and controls would need to cost between ███████████ and ████████████ in order to provide for sufficient profit margins and still be attractive to the end user.

This cost assumes, conservatively, a minimum of 10 units per year with components purchased using blanket order agreements. Purchase of subsystems and major components assume an OEM discount of 20%. The cost would need to include any royalty payments and tooling amortization. Tooling is amortized based on a 5 year life. The cost does not include the laboratory data management system or off-line data analysis software.

2.7 Sales channels

The product will be sold by the existing K-Tron Soder sales channels, with increased focus on the Systems Group for customer interface during sales, system configuration, and startup. Our manufacturers representative network would primarily provide customer identification and preliminary contact only.

2.8 Spare parts, repair

Spare parts must be available for at least 10 years after the last unit sold.

2.9 Patent situation

The current patents related to several of the instruments and the microanalysis techniques thus far employed are the property of General Electric Corporation and will require licensing. We expect to develop further techniques, which are intended to be patented by K-Tron.

3 Technical specifications

3.1 Function requirements

3.1.1 Extruder

The Microcompounder will consist of a 16mm co-rotating twin-screw extruder with its required drive section, electric heaters, and a local chiller for cooling. The extruder will have the following specifications:

- Screw Diameter of 16mm
- Segmented screw and barrel
- Barrel length configurable up to 25:1 L/D
- Split barrel design for easy cleaning
- Screw Speed 0 – 500 rpm
- Dedicated embedded control with Ethernet interface
- Maximum 32 Amp single phase power
- Sheet die at least 15mm wide x 0.10 mm thick
- Material inlet suitable for multiple feeders
- Optional melt pump with drive and controls

- Typical throughput of 5 kg/hr
- Barrel temperature up to 400ºC
- Closed loop temperature control for each zone
- Water supply of less than 5 l/min
- Pressure range 0 to 100 bar
- Motor of at least 1.25 kW
- Closed loop motor control with speed and torque feedback
- Optional atmospheric/vacuum vents
- Optional liquid injection port
- Optional 2.5mm diameter strand die

3.1.2 Feed System

The system will also require from two to four gravimetric microfeeders.   The feeders will be mounted over the inlet of the extruder. The feeders will be chosen based on the required feed rates as well as the characteristics of the material to be fed.

The microfeeders which are currently available are:
- 12mm twin screw feeder
- 10mm single screw feeder
- rotating cone feeder
- vibratory tray feeder

Typically feeder specifications:

- Gravimetric loss-in-weight control
- Embedded control with Ethernet interface
- Changeable screws with various flight configurations and pitches
- At least 20:1 feed rate turndown
- Material contact surfaces of stainless steel or non-reactive plastic
- Maximum 3 Amp single phase power

- Feed rates from 50 to 1000 g/hr
- Digital load cell with 1,000,000:1 resolution
- Closed loop motor control
- Auto feeder calibration function
- Easy to clean design
- Optional venturi vacuum loader for auto refill
- Optional liquid feed system
- Optional gas purge for hopper and seals

Complete specifications for these and other feeders can be found in other K-Tron documents.

3.1.3 Product Handling

As the material exits the extruder the product will have to be automatically collected and prepared for any off-line analysis. This will require the following additional equipment:

- Haul-off with closed loop motor control
- Laser marking system with Ethernet interface
- Optional Temperature controlled water bath
- Optional Strand pelletizer
- Optional Face-cut pelletizer
- Optional Chill roll
- Optional Chill knife

3.1.4 On-line Instrumentation

The on-line instrumentation will be selected and configured based on customer and product requirements. It will be mounted either directly in the melt stream or near the exit of the die. The on-line instrumentation will be used to measure rheological properties, chemical composition, degradation byproducts and color. The on-line instrumentation selection will consist of a rheometer, various spectroscopic sensors, and an "electronic nose".

Rheometer
The on-line rheometer should have the following features:

- Attaches to process using single standard pressure port.
- No waste stream, tested sample returns to the process.
- Simple "in the field' calibration
- Process isolation valve
- Measure melt flow rate or apparent viscosity
- Ethernet connectivity

- Melt Flow Index: 0.1 to 1500 g/10 min
- Viscosity Range: 10 to 10^5 Pa s
- Shear Stress: 3 to 800 KPa
- Shear Rate: 0.1 to 4000 s^{-1} (standard die)
- Dies Available: 1 to 11 mm
- Temperature Range: 40 to 350 ºC
- Pressure Range: 2×10^5 to 3.5×10^7 Pa

Spectroscopic Sensors
The spectroscopic sensors will need to be configured for specific polymer formulations and applications.   The spectral range is typically specified as Ultraviolet (UV), Visible, Near-Infrared (NIR), and Mid-infrared (MIR). Some spectrometers are specified as having an extended range at a higher cost and others are designed to measure a narrow range at a lower cost or with high resolution. The most common ranges for Tier 1 applications will be Visible, for melt flow color measurement, and NIR, for determination of chemical composition. The lighting source must also be specified, if one is required for the application. The light source can supply a wide spectral range, as with tungsten-halogen, or a very narrow spectral range, as with a laser diode.   The probe selection is dependant on the mode of operation. The spectrometer can measure in an absorbance, reflectance, emission, or fluorescence mode. Some of the common requirements for the spectrometers are:

- Fiber optic probe of at least 1m long with integral light source (where applicable)
- Probe construction: 316 stainless steel
- Probe optical interface: sapphire
- Pressure rating: 350 bar
- Temperature rating: 300ºC
- Ethernet connectivity

- Spectral resolution: 2 nm
- Scan speed: 1.8 scans/sec (or better)
- Wavelength accuracy (1σ): 0.5 nm
- Instrument precision (1 σ): 0.01 nm
- Wavelength linearity: 1% of reading
- Spectral Bandwidth: 10 nm +/- 1 nm

Electronic Nose
The "electronic nose" has been shown to have high potential for real time on-line measurements of degradation byproducts, in the form of the volatiles, at the outlet of the extruder die. The electronic nose consists of two components, (1) an array of chemical sensors, in this case they are metal oxide semiconductor gas sensors, and (2) a pattern-recognition algorithm. The sensor array "sniffs" the vapors from the hot polymer and provides

a set of measurements. The pattern-recognizer compares the pattern of the measurements to stored patterns for known materials. Gas sensors tend to have very broad selectivity, responding to many different substances. This is a disadvantage in most applications, but in the electronic nose, it is a definite advantage. Although every sensor in an array may respond to a given chemical, these responses will usually be different. To further complicate the situation the response and recovery times of the individual sensors is different. This requires the use of multivariate analysis tools to provide a suitable pattern recognition approach in order to take into account the responses of all the sensors in the array. This work is ongoing and there is no specification for this instrument at this time.

3.1.5 Off-line Instrumentation

The off-line instrumentation will be selected and configured based on customer and product requirements. It will either be mounted after the material cooling bath and prior to the sample collection system or separate from the compounding system entirely. The off-line instrumentation will primarily be used for the measurement of mechanical properties. It will provide nondestructive measurements, allowing multiple analyses to be made on the same library of samples. The off-line instruments employed will be unique in that they will generally use samples, which are much smaller than typical commercial equipment. The off-line instrumentation selection will consist of a mini biaxial impact tester, indentation tester, static charge dissipation tester, and other commercially available instruments as required. All of the instrumentation described is will need additional development cannot be specified in detail at this time. A brief description of each is given below.

Miniature Biaxial Impact Tester [1]
This technique involved modifying the traditional biaxial impact test so that it could be applied to thin films or ribbons of polymer, and automated to allow rapid testing of the film at successive locations, thereby improving the statistics of the test. Scaled down versions of the conventional biaxial "Dynatup" impact tester were constructed which utilized constant displacement rate rather than a gravity driven dart and samples of extruded polymer films instead of typical 4" diameter, 1/8" thick molded disks. The miniature biaxial test allows discrimination or ranking of materials within the series, and can serve as an initial alternative to conventional testing. The method appears to be a viable alternative to conventional biaxial impact testing for ranking biaxial ductility in polymers during the initial stages of material development.

Indentation Tester [1]
Instrumented indentation involves the recording of a load-displacement curve as a diamond tipped shaft is inserted and then retracted from the surface of a sample. This data can then be analyzed to obtain the elastic modulus, hardness, and work of indentation. With micro-indentation the small size of the indentations means that less material is required for testing which allows for high throughput screening or measurement of mechanical properties either on a series of small samples or across a gradient library.   The prototype experiments showed that indentation elastic modulus could certainly be used to rank order materials, if not measure an accurate value of the modulus. Hardness correlated with yield strength and may be used to rank order polymer strength, but cannot provide a direct, accurate measurement of yield strength. There are commercial suppliers of these instruments which may be contracted as a subsystem supplier.

Static Charge Dissipation Tester [1]
The static decay performance is often evaluated by measuring the time required for an induced charge V_0 to decay by some fraction of its initial value, for example 50% or 90%. We envision that an instrument with an arrangement of multiple samples, along with a data reduction scheme is feasible for measuring the static decay curves for a number of samples simultaneously. Multiple samples can be sequentially moved to position each under the corona charger. After the charging cycle, the samples are then sequentially moved to the measurement position in a repetitive cycle to record the time versus voltage curves. The static decay performance is then evaluated by the value of the curve fit parameters, or an interpolated time value corresponding to a specified degree of voltage dissipation. A working prototype of such a device has been made and an additional alternative design was also diagrammed.

3.1.6 User Interface and Control

The user interface and central control will primarily be PC based, using a commercially available visualization software package. The user interface will be constructed as an extension to the K-Tron Smart Commander system. Specifications of the K-Tron Smart Commander hardware, software and functional capabilities are available in other documents. The operator interface will be the primary interface for all components of the system using a graphical representation of the device where possible. The primary screen will function as the basis for navigation to more detailed information and control of the subsystems and components. The primary screen will provide a graphical representation of the entire system including the microcompounder, feed system, material collection, and marking system. The on-line instrumentation will also be represented on the primary screen. The off-line instrumentation will be referenced on the primary screen as a single entity. Primary operational controls and sensor readings will be shown on the primary screen. All setup and operational parameters for all components will be available on the PC interface through a secondary set screens arranged in a logical fashion. The current K-Tron Smart Commander feeder screens should be used as a model for the interface to subsystems and components. Where applicable, input range limits, alarms, trending, historical data collection, and security should be implemented for each component.

The PC interface will have responsibility for central control and coordination of the system. The user interface will allow for manual control of all system components. However, the primary central control function is to execute a sequential recipe script. The recipe script defines material formulations as well as various machine parameters for the Microcompounding system. Formulation libraries can be generated by the use of existing combinatorial methods and/or design of experiments methods. These tools should be available through a recipe generator. Editing of the recipe should be available through a spreadsheet-like interface. If possible the recipe should be import/export compatible with Microsoft Excel. The recipe will control the material formulations which directly set the throughput of the material and additive feeders. The machine parameters in the recipe script would vary compounder variables such as screw/pump speed, zone temperatures, cooling temperature, haul-off speed, etc. The recipe script will also have control over the sample identification marking system. The recipe script will allow the formulation and machine parameter changes as discrete steps or through a ramping function. Formulation changes can be triggered based on absolute or relative time, values read from one or more sensors/instruments, or based on the output of user programmable function blocks. The user may select any data to be logged and/or plotted during the execution of the recipe, including any output from user programmable function blocks. All data will be time-stamped.

Individual components and sensors may utilize embedded controls and PLCs with integrated digital communication capabilities. The system interconnection will be based on a common protocol for data acquisition, network communication between experimental stations, and data management systems. The assumption is that Ethernet connectivity will be standard.   The central controller will also be responsible for collection of raw data from the off-line instruments either in a manual or automated fashion. Data from these instruments will be integrated into the logged recipe data. Analysis, organization, and archiving of the data and results will be handled externally in a separate networked laboratory data management system.

3.2 Materials of construction / Finish

The design is for general-purpose applications that do not require FDA or USDA compliant materials. Stainless steel surfaces will be at least 2B finish. Mild steel surfaces will be painted K-Tron gray. Any aluminum surfaces will be painted or power coated. Plastics may be used where applicable.

3.3 Environmental conditions

The Combinatorial Compounding System is designed to work in the following environmental conditions without options or modifications:

Storage temperature:	-40...80°C (-40...176°F)
Operating temperature:	15...60°C (59...140°F)
Temperature of feeding goods:	-25...60°C (-13...140°F)
Feeder Purge Pressure:	-50...+50 millibar (-20…+20 inches H_2O) not sealed, may leak
Humidity:	up to 95 % without condensation
Altitude:	< 2000m (< 6500 ft)
Motor Enclosures:	IP 54 / NEMA 12
Electrical Enclosures:	IP 54 / NEMA 12
Feeder and Material Connections:	IP 40 / NEMA 2
Vibrations:	Up to $\pm$ 0.5 m/s² ($\pm$ 0.05 G), 10...50 Hz in all directions

3.4 Standards

Must meet the harmonized standard of CE and UL/CSA.

Generic Electrical Emissions: Industrial	EN50081-2 / IEC 1000-6-2
Generic Electrical Immunity: Industrial	EN50082-2 / IEC 1000-6-2
Low Voltage Directive:	73 / 23 / EWG
ATEX Directive:	Category 3D

Directives and norms related to other explosive or hazardous environments will be applied as required through review by independent testing laboratory, covered under separate project(s).

3.5 Economic considerations

3.5.1 Life expectancy

The expected lifetime is 15 years with proper maintenance, depending upon operating conditions.

3.5.2 Operation safety

According to CE and OSHA standards.

Common tasks, such as removal of covers, require a tool to be performed. A tool-less solution for these operations may be possible but is not recommended. Provisions for a safety stop switch will be implemented. Interlocks will be provided for over temperature, over pressure, and high torque of the extruder. All motors will be protected from output short circuit and motor stall conditions. Interlocks and warnings will provided for any dangerous devices that may be employed such as lasers or x-ray sources.

3.5.3 Commissioning / Maintenance

MTBF:

Mean time between failures for non-moving mechanical components:	15 Years (130,000 hours)
For Moving mechanical components such as shafts, bearings, gears etc:	2 Years (18.000 hours)
For electrical components:	2 Years (18,000 hours)
For SFT (if present)	5 Years (45,000 hours)
For wear parts such as seals:	3,000 hours
For purchased instrumentation and sensors:	Based on manufacturer

MTTR:

Mean time to repair for common wear parts:	$\leq$ 30 Minutes.
For other components:	$\leq$ 90 minutes.

3.6 Documentation

- User manual according to CE standards.
- Internal documents for manufacturing, field service, quality inspection according to ISO procedures.
- Part numbers and bill structures will be defined and implemented by Manufacturing & Engineering using harmonized part numbering system.
- Drawing files for components and assemblies will be provided in native Pro-E format and DXF output.

3.7 Packing

- Extruder will be shipped assembled if possible and screwed on wooden pallet.
- Feeds will be shipped assembled if possible otherwise they will be foamed into cardboard boxes.
- Instruments will be foamed into cardboard boxes for protection.
- Electronics and computers will be foamed into cardboard boxes.
- Boxes will be strapped to a wooden pallet and capped for shipping.

4 Risk analysis

4.1 FMEA

A Failure Mode Effect Analysis is required by the ISO guideline.

4.2 Investments risks

Significant investment is required for a fully capable prototype system.

4.3 Product liability risks

All CE requirements must be fulfilled.

•   A danger analysis must be done
•   Required standards must be fulfilled

5 Appendix

5.1 References

[1] General Electric Yearly Progress Report DE-FC07-01ID14093 July 19, 2002

[2] K-Tron Gravimetric Feeder Specification Sheets

[3] K-Tron Smart Commander Specification

5.2 Related documents

Combinatorial Microcompounding High Throughput Screening Product Development Platform MRD

Combinatorial Microcompounding High Throughput Screening Product Development Platform Project Plan

5.3 Update log

Initial Draft