

REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-05-

0141

data
id

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing information needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Paperwork Reduction Project (0704-0188), Washington, DC 20503

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE January, 2005	3. REPORT TYPE AND DATES COVERED Final Report 01 Feb 2002 - 31 Dec 2004	
4. TITLE AND SUBTITLE Polymer Nanocomposites by Melt Processing			5. FUNDING NUMBERS C-F49620-02-1-0111	
6. AUTHOR(S) D. R. Paul				
6. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Texas Materials Institute University of Texas at Austin Austin TX 78712			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research 4015 Wilson Blvd, Room 713 Arlington, VA 22203-1954 Contract Manager: Dr. Charles Y-C Lee			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for Public Release: Distribution Unlimited				12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 Words) The objective of this project was to establish the basic principles of formation of polymer-organoclay nanocomposites by melt processing techniques and their performance. The key issue is to exfoliate, or disperse, the clay platelets in the polymer so that the highest possible aspect ratio is achieved. It was shown that this depends critically on the extruder type, screw configuration, the structure of the surfactant on the organoclay, and the melt viscosity of the polymer matrix. Very high levels of exfoliation were demonstrated for polyamide systems as determined by quantitative transmission electron microscopy techniques developed as part of this project. The interaction of the organoclay with the polymer is perhaps the most important issue in achieving exfoliation; a qualitative understanding of this interaction was developed which provides some guidance in polymer and organoclay selection. A great deal of effort was devoted to characterizing the morphology or structure of the nanocomposites generated as well as documenting properties like modulus, strength, heat distortion temperature, thermal expansion coefficient, and to a limited extent barrier and flammability. Conventional composite theories seem to give a good description of the reinforcement achieved and can be a useful tool in predicting stiffness and thermal expansion behavior.				
14. SUBJECT TERMS polymers, clay, nanocomposites, mechanical properties, processing			15. NUMBER OF PAGES 20	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

Final Performance Report
on
POLYMER NANOCOMPOSITES BY MELT PROCESSING

AFOSR Agreement: F49620-02-1-0111

Period: February 1, 2002 – December 31, 2004

Principal Investigator: Donald R. Paul
Department of Chemical Engineering
Texas Materials Institute
University of Texas at Austin
Austin, TX 78712

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited



20050414 049

1. Executive Summary

The purpose here is to give a brief overview of the research on nanocomposites accomplished during this three-year project supported by the Air Force Office of Scientific Research.

Background. The research on nanocomposites at the University of Texas at Austin grew from discussions with Southern Clay Products, Inc., located about one hour away, and has involved a close collaboration with them for several years. This connection provides a source of unique clay materials and an invaluable resource for technical expertise in this area. Without this connection much of the work done at UT-Austin would not have been possible. Therefore, our group has a very unique position in this somewhat crowded field. Our early work was sponsored by a one-time, two-year grant from the Texas Advanced Technology Program and then by this three-year grant from AFOSR. From the beginning of our program, we have benefited by a close communication with Dr. Rich Vaia of the Air Force Research Laboratory who has been the principle conduit for making our results useful to Air Force personnel.

Productivity. As of the date of this report, our group has published 15 papers in scientific journals that acknowledge AFOSR support, 3 others are in press; and several more are in various stages of preparation. Our group has given many talks at professional society meetings at many locations in the US, Europe and Asia.

Accomplishments. Our work involves formulation, characterization, and performance of these nanocomposites with the use of modeling to predict structure-property relations. We were among the first to show that high levels of exfoliation of organoclays in polyamides could be achieved by melt processing with performance levels equal to those by the well-known in-situ polymerization process from Toyota. This requires careful selection of extruder type, screw configuration, organic surfactant on the clay, and polymer molecular weight. We have looked at numerous polyamide types (nylon 6; nylon 6,6; nylon 11; nylon 12; etc). We have investigated in depth the formation of nanocomposites based on polycarbonates and have shown that the high

melt processing temperatures required cause significant problems with degradation using conventional surfactants; however, some novel pathways to promising polycarbonate-based nanocomposites have been proposed and will be pursued in future work. We have also explored formation of nanocomposites based on styrene-acrylonitrile copolymers and various polyolefins. In addition to learning how to make nanocomposites from these various polymers, we have devoted a great deal of effort to characterizing their morphology, evaluating their performance with particular emphasis on mechanical properties and linear thermal expansion behavior, and connecting the two via modeling using composite theory. Our work has received a great deal of attention from the scientific community because of the depth of our papers and our attention to important details.

Leverage. Because of the program we have developed with AFOSR support, we have been able to attract other funding and collaborations that contribute to our efforts at no cost to the Air Force. General Motors has been aggressive in commercializing nanocomposites for use in various vehicles as part of a weight reduction strategy for both fuel savings and emissions reduction. GM is currently supporting a post-doc in our labs to measure and model the reduction of linear thermal expansion behavior caused by addition of the clay; this is a critical issue for this and similar applications. We have had three visiting scientists in our lab that came to learn about nanocomposites by participating in our research program. These are all direct benefits to our efforts that became possible because our AFOSR project.

Personnel. This project supported the Ph. D. research of the following students: Timothy D. Fornes, Rhutesh K. Shah, Florencia Chavarria, and Holly Stretz. Others that were involved in the project in various ways included: P. J. Yoon, D. L. Hunter, H. S. Lee, Y. C. Ahn, S. Hotta, U. Gurmendi Lostao, and K. Y. Lee.

2. Introduction and Background

Clay minerals like montmorillonite have been well known and widely used for a very long time. Native clays are hydrophilic and can be dispersed in water.

Organoclays were subsequently introduced to render the clay hydrophobic and dispersible in organic media; major uses are in paints, printing inks, greases, drilling fluids, etc. The organoclays are made by exchanging the alkali-metal ions, typically sodium, that balance the negative charge in the native montmorillonite platelets with organic cations, usually alkyl ammonium salts or surfactants typically derived from natural products. The possibility of dispersing the individual aluminosilicate platelets of clay in polymers, or exfoliation, was brought to the attention of the scientific community in a major way by a series of papers and patents from the Toyota Motor Company describing "polymer-clay hybrids," now more commonly called nanocomposites, made by in situ polymerization of nylon 6 in the presence of clay via a process developed in 1986. These nanocomposites offered the promises of greatly improved performance over that of the matrix polymer in terms of stiffness, strength, heat resistance, barrier properties, flammability, etc.

The possibility of making such nanocomposites by conventional melt processing was first suggested to me by Southern Clay Products, Inc. which resulted in our subsequent long-term collaboration to develop this possibility. Over the last three years, most of this work has been supported by the Air Force Office of Scientific Research. Over the last few years, there has been a tremendous growth in the literature on this subject because at first glance it seems easy to make and characterize nanocomposites; most of these papers have contributed very little to the scientific understanding needed to make a significant technological or commercial impact. We believe our program has dealt with the issues much more deeply and has added to the science base in a meaningful way in large measure because of the knowledge of clay chemistry and the source of a diverse array organoclays we have had access to through Southern Clay Products. Section 7 lists all of the papers published by our laboratory on polymer nanocomposites [1-21], of which [5] through [21] were made possible because of our AFOSR funding; several more will be written in the coming months. Section 5 summarizes briefly the main findings of this work.

It is now clear to us that to date the field of polymer nanocomposites has focused primarily on organoclays that were already commercially available which were designed for other purposes. We have learned a great deal about what can and what cannot be accomplished with these materials. It is our opinion that significant

breakthroughs of technological or commercial significance are possible but they hinge on designing organoclays that improve the interaction of the desired polymer matrix with the organoclay and resolving some of the thermo-oxidation stability problems associated with current surfactants. There is a rich opportunity for further research that is both innovative and in depth; however, we see no value to a flood of papers that continue to appear which offer no new insights or solutions to the current obstacles.

3. Objectives

The objectives of this research are:

- (a) to develop formulation strategies for maximizing the degree of exfoliation of the high aspect-ratio aluminosilicate layers of montmorillonite, MMT, in polymer matrices of technological significance using standard polymer melt processing methodologies by optimizing the organic treatment of the native clay, the processing of the organoclay/polymer mixture, and the nature of the polymer matrix and its interaction with the organoclay;
- (b) to characterize the morphology of these nanocomposites and to understand any important chemical changes such as molecular weight degradation, color formation, etc. that may occur during melt processing using state-of-the-art electron microscopy, x-ray diffraction and scattering;
- (c) to evaluate key physical properties of these nanocomposites to demonstrate and understand the potential opportunities and limitations for achieving superior material performance by this approach. The primary emphasis is on mechanical, thermal, and optical properties.

4. Status of Effort

This three-year project ended on December 31, 2004. All of the objectives mentioned in Section 3 in general terms, as well as the more specific ones described in our proposal, were met. A total of 18 papers and one Ph.D. dissertation, see Section 7, were published or submitted for publication as a result of this project. Three other graduate students, who began their work with support from this project, will continue their work until their dissertations and papers are completed.

5. Accomplishments and New Findings

All of the research accomplished during the course of this project has been described in the publications described in Section 7. The complete methodology used and the resulting data may be found in these publicly available publications. The following is a summary of the key findings with reference to the publication where more information can be found.

- 5.1 We established that nanocomposites based on nylon 6 can be made by melt processing techniques with properties and morphology fully equivalent to those made by the Toyota in situ polymerization process [1].
- 5.2 We showed that the selection of extruder type, screw configuration, and residence time are important variables that must be optimally selected to achieve high levels of organoclay exfoliation [2, 3].
- 5.3 It was demonstrated that matrix molecular weight, or polymer melt viscosity, is an important factor in achieving high levels of exfoliation [4]. High molecular weight nylon 6 leads to better exfoliation than a low molecular weight or injection molding grade. It is believed that the stresses on clay particles can shear them into smaller stacks from which platelets can then be peeled away one by one in the available residence time in the extruder.
- 5.4 Organoclays can be made from a wide variety of amine-based surfactants. We have explored the effect of the molecular structure of the surfactant on the morphology and properties of nanocomposites based on nylon 6 [5, 14], polycarbonate [9], styrene-acrylonitrile copolymers or SAN [21], polyethylene [18] and polyolefin ionomers [20]. The structure of the surfactant can make a huge difference in the degree of exfoliation, and it appears that this structure must be optimized for each matrix since what is best for one is not the best for another.
- 5.5 Our evidence points to a favorable interaction of polyamides with the silicate surface [14]. Minimizing the number of alkyl tails on the surfactant, allows the polyamide more access to the silicate surface and requires the polyamide to mix

with less alkyl segments (an unfavorable interaction) with the result maximizing exfoliation and, hence, properties.

- 5.6 On the other hand, polyolefins do not have affinity for the silicate surface and their mixing with the alkyl tails of the surfactant is a nearly neutral interaction therefore, maximizing the number of alkyls on the surfactant maximizes exfoliation in these cases [18, 20].
- 5.7 It appears that SAN has less affinity for the silicate surface than polyamides and an unfavorable interaction with the alkyls of the surfactant [21]. There are optimum surfactants for the SAN matrix, but none lead to very high levels of exfoliation.
- 5.8 Introduction of polarity into the polyolefin matrix by adding maleic anhydride grafted polyolefin or acid (or neutralized salt) comonomers greatly improves exfoliation in these cases [18, 20].
- 5.9 Polycarbonate is very difficult to form into useful nanocomposites because the commercially available surfactants do not lead to a good organoclay-polymer interaction and these surfactants degrade seriously at the high melt processing temperatures involved leading to matrix degradation and color formation [9, 10]. We are pursuing ideas with a collaborator that may resolve these difficulties.
- 5.10 We have documented that surfactant stability can be a major issue particularly as the processing temperature becomes high. This has been shown in nylon 6 [11] as well as polycarbonate [10]. We are pursuing similar effects in polyolefins. Re-design of surfactants to remedy this situation should be a focus of future work.
- 5.11 We have shown that a properly selected nylon 6 exfoliates an optimal organoclay more efficiently than does nylon 11 and 12 apparently because of the high polarity of nylon 6 [16].
- 5.12 Nylon exfoliates organoclay slightly more effectively than nylon 6,6 [19]. We have shown this is not just the consequence of higher melt processing temperature required. The exact cause has not been precisely determined.
- 5.13 Addition of small amounts of clay leads to an increase in the rate of nylon 6 crystallization because of increased nucleation sites; however, further addition of

clay reduces the rate of crystallization because of mobility issues [7]. The effect of clay on the crystal structure of nylon 6 was studied extensively [7].

- 5.14 Exfoliation of the organoclay is maximized in nylon 6 when a high molecular weight, or high melt viscosity, grade is chosen; however, for injection molding applications, it is necessary to use a low melt viscosity grade to achieve rapid cycle times. A masterbatch process was developed which provides a compromise between these conflicting issues. A high concentration of organoclay masterbatch is made using a high molecular weight nylon 6 which is then let down in a low molecular weight nylon 6 to achieve the final desired content. The performance-processing trade-off as well as implementation of this strategy were described [15].
- 5.15 We collaborated with the staff at the National Institute of Standards and Technology to characterize the morphology of nanocomposites formed from styrene-acrylonitrile copolymers (SAN) formed in our laboratories using a solid state NMR technique developed at NIST; mechanical properties and flammability characteristics were also studied [17].
- 5.16 We collaborated with the University of New South Wales on the interlayer swelling and molecular packing in organoclays [22]. The Australian group provided molecular simulation results while our group provided experimental data and a simple model that unifies the two. These results dispute some earlier notions of how surfactants pack or organize in the galleries of organoclays.
- 5.17 To understand the process of exfoliation or to understand nanocomposite performance, it is essential to have detailed information about the size and aspect ratio of the dispersed nanofiller. We have developed transmission electron microscopy, TEM, techniques for this purpose and have quantified the morphology using semi-automated image analysis techniques [8, 13, 16, 18, 19, 21]. The output is histograms showing frequency of particles versus particle length and platelets per particle from which particle aspect ratio distributions and averages can be determined. While these techniques require a great deal of skill and effort (for meaningful results it is necessary to analyze hundreds of particles), they are essential for meaningful progress in this area. We use these results in modeling

nanocomposite performance. During late 2004 we collaborated with Dr. Rich Vaia and colleagues in image analysis of TEM photomicrographs.

- 5.18 We have measured the linear coefficients of thermal expansion, CTE, in all three coordinate directions for nylon 6 nanocomposites [6]. Addition of clay can dramatically reduce the CTE in the directions in which the clay particles are aligned. Our work in this area led to a collaboration with General Motors on their commercial polyolefin-based nanocomposites used in vehicles for weight reduction.
- 5.19 We have measured mechanical properties for a wide range of nanocomposites including modulus, strength, elongation at break, and impact strength in some cases [1, 4-21]. Such performance is one of the main reasons for interest in nanocomposites so it is essential to determine these properties in a meaningful way. We also find the modulus is one of the best indicators of exfoliation.
- 5.20 We have invested considerable effort in comparing the modulus and CTE with predictions of composite theory; this is not a trivial task because of the quantitative information about composite morphology needed, see 5.17. However, within the limitations of the theory and experiments we find that performance, modulus and CTE, agree rather well with the predictions of conventional composite theory [6, 8]. Thus, composite theory can be a useful tool for designing nanocomposites. There are many beneficial effects of using nanoscale fillers; however, the mechanism of reinforcement appears to be essentially the same as in conventional fillers.
- 5.21 Some effort was devoted to exploring how the source of the clay itself affects exfoliation and nanocomposite performance [10, 13]. There is a need for additional work in this area particularly as synthetic clays become more widely available.

6. Personnel

The following people received financial support from this project:

Donald R. Paul	Faculty
Timothy D. Fornes	Graduate Student
Rhutesh K. Shah	Graduate Student

Florencia Chavarria Graduate Student
Holly Stretz Graduate Student

The following people contributed to this project but were supported by other means:

P.J. Yoon
D.L. Hunter
H.S. Lee
Y.C. Ahn
S. Hotta
U. Gurmendi Lostao
K.Y. Lee

7. Publications

- [1] J. W. Cho and D. R. Paul, "Nylon 6 Nanocomposites by Melt Compounding," *Polymer*, **42**, 1083 (2001)
- [2] H. R. Dennis, D. L. Hunter, D. Chang, S. Kim, J. L. White, J. W. Cho, and D. R. Paul, "Nanocomposites: The Importance of Processing," *Plastics Engineering*, **57**, 56 (2001).
- [3] H. R. Dennis, D. L. Hunter, D. Chang, S. Kim, J. L. White, J. W. Cho, and D. R. Paul, "Effect of Melt Processing Conditions on the Extent of Exfoliation in Organoclay-Based Nanocomposites," *Polymer*, **42**, 9513 (2001).
- [4] T. D. Fornes, P. J. Yoon, H. Keskkula, and D. R. Paul, "Nylon 6 Nanocomposites: The Effect of Matrix Molecular Weight," *Polymer*, **42**, 9929 (2001).
- [5] T. D. Fornes, P. J. Yoon, D. L. Hunter, H. Keskkula, and D. R. Paul, "Effect of Organoclay Structure on Nylon 6 Nanocomposite Morphology and Properties," *Polymer*, **43**, 5915 (2002).
- [6] P. J. Yoon, T. D. Fornes, and D. R. Paul, "Thermal Expansion Behavior of Nylon 6 Nanocomposites," *Polymer*, **43**, 6727 (2002).
- [7] T. D. Fornes and D. R. Paul, "Crystallization Behavior of Nylon 6 Nanocomposites," *Polymer* **44**, 3945 (2003).
- [8] T. D. Fornes and D. R. Paul, "Modeling Properties of Nylon 6/Clay Nanocomposites Using Composite Theories," *Polymer*, **44**, 4993 (2003).
- [9] P. J. Yoon, D. L. Hunter, and D. R. Paul, "Polycarbonate Nanocomposites: 1. Effect of Organoclay Structure on Morphology and Properties," *Polymer*, **44**, 5323 (2003).

- [10] P. J. Yoon, D. L. Hunter, and D. R. Paul, "Polycarbonate Nanocomposites: 2. Degradation and Color Formation," *Polymer*, **44**, 5341 (2003).
- [11] T. D. Fornes, P. J. Yoon, and D. R. Paul, "Polymer Matrix Degradation and Color Formation in Melt Processed Nylon 6-Clay Nanocomposites," *Polymer*, **44**, 7545 (2003).
- [12] T. D. Fornes and D. R. Paul, "Formation and Properties of Nylon 6 Nanocomposites, *Polimeros: Ciencia e Tecnologia*, **13**, 212 (2003).
- [13] T. D. Fornes, D. L. Hunter, and D. R. Paul, "Effect of Sodium Montmorillonite Source on Nylon 6/Clay Nanocomposites," *Polymer*, **45**, 2321 (2004).
- [14] T. D. Fornes, D. L. Hunter, and D. R. Paul, "Nylon-6 Nanocomposites from Alkylammonium-Modified Clay: The Role of the Alkyl Tails on Exfoliation," *Macromolecules*, **37**, 1793 (2004).
- [15] R. K. Shah and D. R. Paul, "Nylon 6 Nanocomposites Prepared by a Melt Mixing Masterbatch Process," *Polymer*, **45**, 2991 (2004).
- [16] T. D. Fornes and D. R. Paul, "Structure and Properties of Nanocomposites Based on Nylon 11 and 12 Compared with Those Based on Nylon 6," *Macromolecules*, **37**, 7698 (2004).
- [17] S. Bourbigot, D. Vanderhart, J. Gilman, H. A. Stretz, and D. R. Paul, "Solid State NMR Characterization and Flammability of Styrene-Acrylonitrile Copolymer Montmorillonite Nanocomposites," *Polymer*, **45**, 7627 (2004).
- [18] S. Hotta and D. R. Paul, "Nanocomposites Formed from Linear Low Density Polyethylene and Organoclays," *Polymer*, **45**, 7639 (2004).
- [19] F. Chavarria and D. R. Paul, "Comparison of Nanocomposites Based on Nylon 6 and Nylon 6,6," *Polymer*, **45**, 8501 (2004).
- [20] R. K. Shah, D. L. Hunter, and D. R. Paul, "Nanocomposites from poly(ethylene-co-methacrylic acid) Ionomers: Effect of Surfactant Structure on Morphology and Properties," *Polymer*, submitted.
- [21] H. A. Stretz, D. R. Paul, R. Li, H. Keskkula, and P. E. Cassidy, "Intercalation and Exfoliation Relationships in Melt-processed Poly(styrene-co-acrylonitrile)/Montmorillonite Nanocomposites," *Polymer*, submitted.
- [22] D. R. Paul, Q. H. Zeng, A. B. Yu, and G. Q. Lu, "The Swelling and Molecular Packing in Organoclays," *Chem. Mater.*, submitted.

Of the above, [5] through [23] were made possible by this AFOSR funding. Several other papers are in the planning stages and will be completed in the coming months.

One measure of the impact of our work in this rapidly emerging area is the number of downloads of our published papers by interested readers in a given period of time. Such information is not usually available, but the publisher of Polymer has informed us that during 2003, paper number [7] above was downloaded 834 times while [8] was downloaded 890 times which places both within the top ten most frequently downloaded papers from this journal during this period.

8. Interactions and Transitions

(a) Presentations made during the period of this project:

D. R. Paul, "Polymer Nanocomposites by Melt Processing," seminar given in Department of Polymer Science at the University of Akron, Feb. 28, 2002.

D. R. Paul, "Polymer Nanocomposites by Melt Processing," seminar given in Department of Macromolecular Science at Case-Western Reserve University, Mar. 1, 2002.

D. R. Paul, "Polymer Nanocomposites by Melt Processing," invited talk in the Symposium on Polymer Nanocomposites at the Materials Research Society meeting in San Francisco, Apr. 3, 2002.

D. R. Paul, "Polymer Nanocomposites by Melt Processing," seminar given at ExxonMobil Corporate Research Laboratory, Clinton, NJ, Apr. 11, 2002.

D. R. Paul, "Polymer Nanocomposites by Melt Processing," seminar given in Department of Chemistry, University of Toronto, July 25, 2002.

D. R. Paul, "Polymer Nanocomposites by Melt Processing," seminar given in Department of Chemical Engineering at the University of Alberta, Aug. 9, 2002.

T. D. Fornes, "Effect of Organoclay Structure on Nylon 6 Nanocomposite Morphology and Properties," paper given at American Chemical Society meeting, Boston, Aug. 18, 2002.

D. R. Paul, "Thermal Expansion Behavior of Nylon 6 Nanocomposites," paper given at American Chemical Society meeting, Boston, Aug. 20, 2002.

D. R. Paul, "Polymer Nanocomposites by Melt Processing," lecture given at Mumbai University Institute of Chemical Technology, Mumbai, India, Mar. 10, 2003.

D. R. Paul, "Polymer Nanocomposites by Melt Processing," lecture given at National Chemical Laboratory in Pune, India, Mar. 12, 2003.

D. R. Paul, "Polymer Nanocomposites," lecture given at Local Section Meeting of the Society of Plastics Engineers, Austin, Texas, Nov. 21, 2002.

D. R. Paul, "Polymer Nanocomposites by Melt Processing," seminar given at Dept. of Mechanical Engineering, Texas A&M University, College Station, Texas, Oct. 16, 2002.

D. R. Paul, "Polymer Nanocomposites by Melt Processing," seminar given at Dept. of Chemical Engineering, Iowa State University, Ames, Iowa, Oct. 24, 2002.

D. R. Paul, "Polymer Nanocomposites by Melt Processing," seminar given at School of Textile and Fiber Engineering, Georgia Institute of Technology, Atlanta, Georgia, Apr. 7, 2003.

D. R. Paul, "Polymer Nanocomposites," lecture given at Bayer Corporation in Pittsburgh, Pennsylvania, Aug. 21, 2003.

D. R. Paul, "Polymer Nanocomposites," lecture given at Centro de Investigacion en Quimica Aplicada, Saltillo, Mexico, Aug. 14, 2003.

D. R. Paul, "Properties of Well-Exfoliated Polymer/Clay Nanocomposites: Comparison of Experiment with Theory," lecture given at Commonwealth Scientific and Industrial Research Organization (CSIRO) in Melbourne, Australia, July 10, 2003.

D. R. Paul, "Properties of Well-Exfoliated Polymer/Clay Nanocomposites: Comparison of Experiment with Theory," lecture given at Center for Advanced Materials Technology, University of Sydney, Sydney, Australia, July 15, 2003.

D. R. Paul, "Polymer Nanocomposites," Invited Lecture given at New Polymeric Materials: An International Symposium on synthesis, Characterization, Processing and Applications of Polymers," Capri, Italy, Oct. 23, 2003.

D. R. Paul, "Polymer Nanocomposites," Plenary Lecture given at the 7th Brazilian Polymer Conference," Belo Horizonte, Brazil, Nov. 10, 2003.

D. R. Paul, "Revolution in Engineering Polymers," Invited Lecture given at Industrial Research Institute's 2004 Frontiers of Technology, San Ramon, CA, Mar. 3, 2004

D. R. Paul, "Polymer Nanocomposites," paper given at American Chemical Society meeting, Anaheim, CA, Mar. 29, 2004.

D. R. Paul, "Insights into the Formation and Properties of Well-Exfoliated Nanocomposites," Invited Paper given at the Society of Plastics Engineers Annual Technical Conference (ANTEC), Chicago, IL, May 17, 2004.

D. R. Paul, "Polymer Nanocomposites by Melt Processing: Structure and Properties," Invited Lecture given at the Council for Chemical Research NICHE

Conference: Synthesis and Characterization of Customized Nanocomposites and Materials," St. Pete Beach, FL, June 2, 2004.

D. R. Paul, "Structure and Properties of Polymer Nanocomposites," Invited Lecture given at the IUPAC World Polymer Congress, MACRO 2004, Paris, France, July 7, 2004.

D. R. Paul, "Properties of Well-Exfoliated Polymer/Clay Nanocomposites: Comparison of Experiment with Theory," Plenary Lecture given at the XIII International Materials Research Congress, Cancun, MX, Aug. 23, 2004.

D. R. Paul, "Polymer Nanocomposites: Structure and Properties," Seminar at 3M Corporation, Austin, TX, Aug. 10, 2004.

D. R. Paul, "Polymer Nanocomposites: Structure and Properties," Seminar at Bridgestone Corp., Yokohama, Japan, Sept. 16, 2004.

D. R. Paul, "Polymer Nanocomposites: Structure and Properties," Seminar at Mitsubishi Engineering Plastics, Hiratsuka, Japan, Sept. 16, 2004.

D. R. Paul, "Polymer Nanocomposites: Structure and Properties," Seminar at Chinese Academy of Sciences, Changchun Institute of Applied Chemistry, Changchun, China, Sept. 20, 2004.

D. R. Paul, "Polymer Nanocomposites: Structure and Properties," Seminar at Jilin University, Jilin, China, Sept. 22, 2004

D. R. Paul, "Polymer Nanocomposites: Structure and Properties," Seminar at Chinese Academy of Sciences, Institute of Chemistry, Beijing, China, Sept. 24, 2004.

D. R. Paul, "Polymer Nanocomposites: Structure and Properties," Seminar at Kraton Polymers, Houston, TX, Sept. 6, 2004.

D. R. Paul, "Polymer Nanocomposites: Structure and Properties," Seminar at Kuraray America, Inc. Pasadena, TX, Sept. 7, 2004.

D. R. Paul, "Polymer Nanocomposites: Structure and Properties," Plenary Lecture at Annual meeting of the American Institute of Chemical Engineers, Austin, TX, Nov. 10, 2004.

(b) During the period of this project we provided the following consultations and advice:

- Through a series of electronic messages and conference calls in April and May of 2002, we provided assistance to Dr. Richard A. Vaia of the Air Force Research Laboratory and one of his collaborators, Elena Vasiliu, in developing techniques for measuring gas permeation in nanocomposite materials.
- We have had numerous contacts with the group at MIT during 2002, especially Greg Rutledge and Mary Boyce, regarding the modulus of montmorillonite platelets and other issues.
- We have had a series of exchanges with ExxonMobil about how to form nanocomposites by melt processing; we have given them assistance that will help their beginning research program. I visited their Clinton laboratory on April 11, 2002 (host = Hubert King), and on June 17, 2002, Pat Brant and Caiguo Gong of Baytown visited our laboratory. I have visited ExxonMobil several other times.
- We have a continuous collaboration with Southern Clay Products, Inc. located one hour from Austin. Our primary contact is Dr. D. L. Hunter. They visit our laboratories often and we visit theirs. The exchanges are primarily technical and relate mainly to organoclay chemistry; however, we assist them in devising strategies for commercial development and implementation of nanocomposites. In turn, our help to them is passed on to their customers interested in using SCP clay materials. For example, in 2003 we had some very complementary feedback from Henrik Eriksson of Polykemi AB in Sweden regarding information generated in our lab.

- Our recent work on modeling the mechanical properties of nanocomposites using composite theories (see paper #8 in Section 7) has been reduced to a convenient spreadsheet format which can be easily used for such calculations. This software has been provided to Air Force personnel, several university groups, and various companies. Southern Clay Products and General Motors have made extensive use of this tool.
- Since early in 2002, we have had a series of discussions with General Motors (William R. Rodgers) regarding our nanocomposite research and how it can be useful as they continue to introduce these materials into commercial use for automotive applications. GM is aggressively pursuing commercial use of nanocomposites for the primary purpose of reducing vehicle weight for fuel economy. We have entered into a collaborative research program with them primarily in the area of improving dimensional stability (or reduction in thermal expansion) through addition of organoclay fillers to polymers. They are supporting a post-doctoral fellow (Hyuk-soo Lee) in our laboratory. We have a continuous flow of information and results to GM personnel and their other university collaborator Prof. Christopher Macosko at the University of Minnesota.
- We have had numerous discussions with Prof. William Brittain at the University of Akron (also a member of the MIT DURENT team) in two areas. One is in preparation of nanocomposite films for permeation measurements. The other is a novel concept of organically modifying clays using polycaprolactone chains for better compatibility with polymers like polycarbonate, ABS, PVC, etc.
- We have had discussions with Prof. Gary Beall of Texas State University regarding novel surface treatments of clay.
- An exchange student (Urko Gurmendi Lostao) in the Ph.D. program at the University of the Basque Country (San Sebastian, Spain) spent six months in our labs participating in this project. He developed some results that have been helpful in better understanding polymer-clay interactions using model compounds. We hope to continue this collaboration as part of his program back in Spain.

- In 2004 we had extensive discussion with Southern Clay Products, Ramanan Krishnamoorti of the University of Houston, and Hung-Jue Sue of Texas A&M about establishing a consortium among our institutions for making a step advance in understanding of how to achieve better exfoliation of organoclays, particularly in polyolefins.
- We have interacted with Mitsubishi Engineering Plastics in the area of nanocomposites based on polycarbonate. Yoshi Kayano of their research laboratories is our main contact person. I shared our results in this area with Kayano during his visits to Austin; I visited their facilities in Japan in September 2004 for broader discussions. They have provided us with some financial support.
- During a visit to Australia in 2003, I had extensive discussions with the staff at the National laboratory CSIRO in Melbourne (Anita Hill) regarding mutual interests in nanocomposites. We have developed a broad plan for collaboration via a UT-CSIRO Memorandum of Understanding (MOU) a part of which involves nanocomposites. As a first step, they are in the process of preparing a series of clays with altered charge density or cation exchange capacity (CEC) for our use in determining the role of CEC in exfoliation of organoclays in various matrices like nylon 6 and polypropylene.
- Early in 2003 we began discussions with Asahi Kasei Corp. in Japan (contact: T. Tanabe) regarding their interest in the work on nanocomposites going on in our laboratories. As a result, they sent one of their researchers (Sachio Hotta) to work with our group with a specific interest in polyethylene-based nanocomposites. Hotta stayed in our laboratory for one year and has now returned to Japan. A paper based on his work has been published.
- During 2004 we developed a working relationship with the Institute for Chemical Engineering and Science (ICES) in Singapore (contact is P.K. Wong). They have the expertise to synthesize some specialized organoclays that we proposed for improving exfoliation and chemical stability in polycarbonate. They will send these organoclays to us for processing and evaluation of the nanocomposites.

- We collaborated with Dr. J. W. Gilman and colleagues at the National Institute of Standards and Technology on styrene-acrylonitrile copolymer nanocomposites. This resulted in one joint publication.
- We collaborated with Prof. A. B. Yu at the University of New South Wales on swelling and molecular packing in organoclays. This resulted in one joint paper submitted for publication.

(c) Transitions during the period of this project:

We have relatively frequent contacts on many topics with Dr. Richard A. Vaia of the Air Force Research Laboratory. We feel that this has been the best route for transitioning knowledge generated in our laboratory into the Air Force. He visited our laboratory in 2004.

As mentioned in (b) above, we have rather extensive contacts with industry that will be valuable in transitioning our knowledge base to the private sector. Of these contacts, the one with Southern Clay Products, Inc. (Dr. D. L. Hunter is the primary contact) is clearly the most well developed and likely to have the most impact. Southern Clay Products works with many companies having current or potential interests in commercial use of nanocomposite technology. Our almost daily contact and collaboration with Dr. D. L. Hunter means that results from our laboratory find their way to many companies on a nearly continuous basis.

Timothy D. Fornes [Ph.D. from our laboratory] is currently completing a post-doctoral assignment with Prof. Ned Thomas of MIT.

P. J. Yoon [Post-doctoral fellow from our laboratory] has accepted employment with Southern Clay Products, Inc.

9. New Discoveries, Inventions, or Patent Disclosures

None.

10. Honors and Awards

During this project I was selected to give a Plenary Lecture at the 7th Brazilian Polymer Conference in Belo Horizonte and an Invited Lecture at MACRO 2004 (INPAC) in Paris on our work on nanocomposites.

The following is a list of lifetime achievement honors (other than society awards).

- | | |
|------|--|
| 1988 | Elected to National Academy of Engineering |
| 1994 | Named a Distinguished Engineering Alumnus of North Carolina State University |
| 1995 | Elected Fellow of American Institute of Chemical Engineers |
| 2000 | Distinguished Service Citation from the University of Wisconsin |
| 2000 | Elected as Corresponding Member of the Mexican Academy of Sciences |
| 2000 | Elected Fellow of the Polymeric Materials: Science and Engineering Division of the American Chemical Society |
| 2004 | Elected Fellow of Society of Plastics Engineers |

Over 20,500 citations to our research papers were listed by Science Citations Index at the end of 2003.

Listed as #135 in 1000 Most Cited Chemists 1981-1997 (see <http://www.ill.fr/dif/citations/chemists.html>).

Listed by ISI Web of Science as a Highly Cited Research both in Materials Science (total of 224 worldwide researchers listed in this category) and in Chemistry (total of 217 listed) (see <http://isihighlycited.com/>).