THE UTILIZATION OF FILLERS AND REINFORCEMENTS TO DEVELOP AN OPTIMAL DAP MOLDING COMPOUND

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ABSTRACT

Diallyl phthalate (DAP) resin-based compounds were formulated and tested. In these formulations, various types of fillers and fiberglass reinforcements were used in different concentrations while taking into consideration packing concepts, optimum aspect (L/D) ratios, resin content, rheology of the molding compound, and ultimately, the compound's performance. These formulations were required for transfer molding without restricting the melt flow through a gate size of less than 1 mm. The end products are very small parts that must conform to stringent dimensional tolerances (typically ± 0.05 mm) and exhibit physical properties that exceed the requirements specified by MIL-M-14G without compromising excellent electrical characteristics. These objectives were achieved by changing from chopped glass roving to screened, milled fiberglass, by the use of microspherical fillers, and by improving micro packing which allowed an increase in the total fiber/reinforcement loading.

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DISCLAIMER

INTRODUCTION

EG&G Mound Applied Technologies (Mound) has a number of applications for high quality molding compounds that will mold well and retain small metallic electric conductors, while maintaining good dielectric properties. Most of the properties are specified by MIL-M-14G, which designates a DAP (diallyl phthalate) compound, but does not specify material formulation or processing.

Because vendor-purchased DAP molding compounds were proprietary, there was a concern that an additive may adversely affect long term compatibility. Although the initial incoming batches were analyzed and characterized for compatibility, vendor formulation changes could occur without the user's permission or awareness. Therefore, small batch, in-house, custom formulation became a prime consideration. Mound had already demonstrated the ability to formulate DAP molding compounds and was producing Orlon (R) and asbestos filled varieties.

To achieve this undertaking, Mound enlisted the expertise of Dr. J. V. Milewski, an independent consultant formerly with Los Alamos National Laboratories, and H. S. Katz of Utilities Development Corporation. This project began with initial attempts to process a formulation similar to that provided by vendors. This would eliminate variations in the fillers and reinforcements used by different vendors and any batch-to-batch variation by the same vendor. In addition, by producing the formulation in-house, any concern over contaminants or other additives that would cause long term compatibility problems could be eliminated.

The initial efforts to formulate the DAP molding compound demonstrated the dynamic nature of this material and its sensitivity to various filler and reinforcement type and content. During the formulation development, it became evident that batches that could be formulated to meet MIL-14-G often differed significantly under specific applications and molding parameters.

The basis for improvement of DAP molding compounds was to study three major areas: the formulation ingredients, the application of good packing theory, and the selection of appropriate processing methods. The goal was to determine the optimal formulation and establish a processing method that preserves fiber aspect ratios to a sufficient extent that good reinforcement is achieved. Fibers that are initially too long have a tendency to clump and bundle during processing, causing poor rheology, resin-rich areas, and voids in the composite.

OBJECTIVE AND CONSTRAINTS

The objective of this project was to improve the physical properties of the DAP molding compound so that it would consistently test significantly higher than the specified values of MIL-M-14G. This would be achieved by optimizing the fiberglass, fillers, fiber/filler ratio, and processing of the DAP molding compound. The improvements in these test values had to be coupled with good flow and processing characteristics of the molding compound as well as the maintenance of excellent electrical properties in the molded products. The ultimate demonstration of improved processing characteristics would be the establishment of a formulation that would perform according to specific part requirements, but be less sensitive to aging and slight variations in molding process parameters.

To establish a baseline for this development effort, five test criteria were selected from the specification (Table 1) for assessment of vendor-supplied material and early Mound-processed formulations. As the project continued to evolve, these tests were performed on each batch of material to determine the progress being made.

Certain conditions and constraints should be stated before the specific formulation and results are discussed. First, the test parameters evaluated were chosen because they had legitimate correlation to the specific application under consideration. These properties are also interrelated; maximizing one value will often affect one or more of the others. It has been the intent, therefore, to achieve the highest overall results, ensuring that each test result meet or exceed the industry standard. The results of this project indicated that if the application required an increase in one specific area, such as tensile strength, a formulation could be designed to maximize this value while holding the other test criteria at the minimum requirements of MIL-M-14G.

Another consideration that was paramount to our application was the moldability requirements. With gate sizes below 1 mm, the particle size and configuration of fillers and reinforcements added had a definite effect on the compound's processability. There is evidence that, without this application constraint, significantly higher results could be achieved.

The types of fillers and reinforcements that could be used were also restricted because of the long term compatibility requirements for these specific applications and their role in the system. Although the details will not be addressed here, only constituents with demonstrated compatibility could be used in this compound.

Finally, batches that appeared promising were molded in the exact configuration used in production applications and then evaluated. The information from this evaluation was used to determine which modifications would be attempted on subsequent batches. This biased the results toward one specific molding technique and part configuration.

EXPERIMENTAL

Screening of the Fibers

Treated fiberglass, Fiber Tech 9174, was evaluated to determine the optimum aspect ratio for the glass fibers. The fiberglass was screened through sieves of 50, 100, and 200 mesh by using a Ro-tap sieve shaker, Model B (commercial orbital/vibratory device) for 10, 20 and 30 min. The results of the screening are summarized in Table 2. From the table, it is evident that the results will vary depending on the energy and the time used during the process of screening the fibers. It was obvious that the clumps and bundles from the +50 mesh screen (Figure 1) were too large for this project's application. Photo micrographs of the glass fibers from the +100, +200 and -200 mesh screenings are shown in Figures 2-4, respectively. It is interesting to note that, even after screening, small fragments (fines) are present and some clumping appears. For this formulation, screening for 20 min using the +100 or +200 mesh did the best job of eliminating the fines and producing short fibers with minimal clumping.

Measuring the L/D Ratio of the Screened Fibers

The L/D ratios of these fibers was determined by measuring their bulk volume. This was done by weighing a quantity (10 g) of each screened fraction and placing it in a separate 100-mL measuring cylinder. The cylinder was then tapped lightly three or four times and the volume occupied was noted. The relative bulk volume was then correlated with the L/D ratios of the fibers by using the curve shown in Figure 5 [1]. These results are summarized in Table 3.

Preparing the Molding Compound

The processing of DAP formulations was performed at two sites: E G & G Mound Applied Technologies (Mound) and Utility Development Corporation (UDC). This parallel effort allowed subtle processing changes to be evaluated to determine their relative impact.

The basic compounding techniques used by UDC involved the use of a ball mill to disperse the clay, pigments, and stearates before they were added to the formulation. The specific technique involved ball milling for a minimum of 3 hr in 200 g of methyl ethyl ketone (MEK) and 400 g of acetone. A 1% solution of hydroquinone was prepared separately in acetone. The dispersed pigment/stearate blend was then added to the DAP solution along with the remaining fillers. The glass fiber was added and mixed until the fiber was uniformly wetted. The mix was then partially dried, and the tacky mixture placed in a sigma blade mixer to individualize and wet the glass fibers.

The high shear of the sigma mixer quickly separates the individual glass filaments and then begins chopping and reducing the aspect ratio of the fibers. It has been determined that extensive processing can sharply reduce the aspect ratio and should, therefore, be limited to the minimum required to obtain good fiber wetting.

The compound was then dried by spreading out a thin layer on a polypropylene screen. Settling of the glass spheres and fibers was a concern during the drying of the compound. With several of the early batches, a lighter color was observed on the bottom of the molding compound layer after it was spread out and dried. When the molding compound was examined closely, it was obvious that the lower layer of material had a higher concentration of glass, producing the lighter color. This had a detrimental affect on the molding properties. The light areas had a poor surface profile indicating the resin concentration in these areas was not sufficient to fully wet the fiber.

This situation was eliminated by spreading out the thin layer on a polypropylene screen and periodically flipping the flat spread compound over while it dried. This resulted in a very uniformly colored compound with no preferential settling.

It was noted that irregularities in color can also be attributed to inadequate dispersion of the clay and alumina trihydrate, which contributes some white to the final compound and increases the opacity of the small percentage of titanium dioxide.

The Mound processing initially focused on chopped strand fiberglass as the major reinforcement material, and formulation equipment and techniques were selected accordingly. Based on published results of mixer manufacturers' tests, the horizontal plow blade mixer was selected [2]. Because of this equipment's availability, it was used for all of the processing runs performed at Mound.

Another major processing difference concerned the layered drying and "B-staging" performed at UDC versus the roll milling (calendaring) and rotary drying performed at Mound. It was determined that excessive roll milling reduced glass fiber length, and that this adversely affected physical properties. However, it was also demonstrated that the roll mill was very effective in accomplishing good dispersion of glass fibers, including the milled glass fibers that were in clumps after the screening process. The production formulation processing was, therefore, modified to minimize the damage to the glass fibers during roll-milling, yet still accomplish uniform glass dispersion and acetone evaporation.

Molding

The samples were compression-molded into standard discs (5 cm diameter by 0.3125 cm thickness) and bars (1.25 cm square by 12.5 cm long). The samples were molded at 150°C using a Carver press and a standard bumping cycle ranging up to 20.68 M Pa.

Testing

Adhering to the American Society for Testing and Materials (ASTM) specified methods, the following tests were performed on the samples:

- Compressive properties, D695
- Tensile strength, D651
- Arc resistance, D495
- Deflection temperature, D648
- Impact resistance, D256

RESULTS AND DISCUSSION

Analysis of the formulation revealed that the performance of the molding compound could be improved by the application of packing concepts. The early formulations primarily relied on 1/8-in. chopped glass fibers in the matrix to provide mechanical strength. In that size and form, when high percentage loadings are used, the fibers may restrict flow or undergo severe breakage while flowing through very small gates and into the fine details of the mold cavity and metal inserts. Processing of the compound can also result in a drastic reduction of the aspect ratio, and produce a large amount of sharp, broken glass debris. Shorter fibers created a compound with improved moldability, but the molded parts were marginal in performance. This could be attributed to the large amount of fibers below the critical aspect ratio, which do not provide any reinforcement, and to the sharp, broken glass debris, which significantly reduces the mechanical properties. The size and ratio of the fiber/filler combination for this formulation was far from the optimal for good theoretical packing. This adversely affected the rheological and flow properties and produced inconsistencies in the molded pieceparts.

The source of this problem was that the chopped glass fibers were initially too long and had to be broken down during subsequent processing to make the compound moldable (specifically for micro-molding operations). To overcome this situation, the use of milled fiberglass that was previously screened for controlled aspect ratio was incorporated.

Using screened fibers that are shorter and more consistently sized produced superior mixing and flow properties with less fiber damage. This higher survival ratio yields more intact glass fibers for reinforcement and a reduction in the amount of the damaging, sharp, broken glass debris in the product.

In addition, one vendor-supplied formulation contained calcium carbonate and, although this filler is widely used, it was eliminated from consideration because of its potential moisture sensitivity and the possible resulting detrimental affects on electrical properties, especially in humid conditions.

The compound formulation was also changed by reducing some of the "irregular-shaped" alumina trihydrate filler and replacing it with smooth glass beads of a size chosen to improve micropacking. The beads also improve the mixing and subsequent dispersion of the fibers, limiting the tendency of additional breakup and improving overall flow and molding characteristics.

The amount of catalyst present in the initial batches was also reviewed. In some systems, excess peroxide can cause chain growth termination before the optimum molecular weight is achieved. This excessive initiator can also lead to accelerated thermal decomposition by increasing the generation of free radicals at high end-use temperatures. Also, the remaining peroxide acts as a plasticizer and can lower the heat deflection temperature of a thermoset. Therefore, the peroxide concentrations were slightly reduced in order to enhance the formulation performance.

It was determined that, in addition to the compound constituents, the processing techniques used during the formulation could affect the physical properties of the DAP. To obtain the maximum physical properties in a filled system, it is essential that the filler be properly dispersed. If this does not occur, unwetted filler agglomerates will create localized stress points in the molded composite and cause premature failure.

CONCLUSIONS

The objective of this undertaking was to develop a DAP molding compound that would outperform the requirements of MIL-M-14G, be less parameter sensitive, and flow through small gates. An additional constraint was that candidate fillers and reinforcements had to meet the compatibility requirements of Mound's specific molding application.

In all, over 35 batches of molding compound (mostly small, development size batches) were formulated and tested. Table 2 shows the properties of some of the best formulations to date along with the values for typical vendor-supplied batches for comparison purposes. Each of the evaluation batches listed met or exceeded each of the test criteria specified in MIL-M-14G. The data for each batch were then normalized by dividing the test criteria value by the specification value. This information is displayed graphically by individual, normalized attributes in Figure 2, and by the normalized averages in Figure 3. The data were then evaluated using several weighting schemes to emphasize different criteria and to attempt to downplay the contribution of an individual parameter that is uncharacteristically high.

It has been demonstrated that standard DAP formulations can be significantly improved by using a systematic, scientific approach. This was accomplished by the following methods: applying packing concepts, evaluating resin-to-solids ratio, and determining the optimal aspect ratio. Constituent selection and synergy were also important factors in the development of this compound. In addition, there were several processing techniques that were determined to be critical, and subsequent modifications further enhanced the performance of the formulation.

In conclusion, by the application of the aforementioned techniques, formulations have been defined which possess exceptional performance characteristics in the categories tested. These categories were tensile strength, compressive strength, Izod impact, heat distortion and arc resistance. As a result of this project, batches can be custom-formulated to enhance their performance in one specific category or to produce across-the-board improvement.

REFERENCES

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BIOGRAPHICAL SKETCHES

Christopher J. Kaye, a senior product engineer at EG&G Mound Applied Technologies, received his Bachelor of Science degree in industrial and systems engineering and a Master of Science degree in engineering management from the University of Dayton. Mr. Kaye spent three years as quality control engineer at Monsanto Research Corporation, Mound Facility, before accepting a job in product engineering. His current responsibilities include overall manufacturing coordination of plastic molded components, assisting in the development of an optimum molding compound, new plastics applications, and the management of five programs from prototype to full production including documentation, fabrication, inspection, and testing.

Harry S. Katz has over 35 years experience in research, development, and production of plastics and composite materials. He holds eight U.S. patents and a number of foreign patents on plastics, composites, and improved processing methods. Mr. Katz is the author of many articles on composites and has been the director of many seminars in this field. His company, Utility Development Corporation, has completed many R & D programs for industrial firms and government agencies. A member of numerous professional organizations, Mr. Katz is co-editor of the *Handbook of Reinforcements for Plastics* and the *Handbook of Fillers for Plastics.*

John V. Milewski has been in the field of advanced materials and composites for more than 38 years. Currently a consultant on the development and use of advanced materials and composites, he is an internationally recognized expert in the areas of whiskers, short fiber fillers, and the packing concept. Dr. Milewski played a key role in the use of new materials in rockets, co-founded the world's first commercial producer of whiskers, and developed Los Alamos National Laboratory's highly successful VLS sililcon carbide whisker growth and ceramic material composite programs. He holds 24 patents and is the co-editor of the *Handbook of Reinforcements for Plastics* and the *Handbook of Fillers for Plastics*.

Robert Schneider is a member of the technical staff in the Organic Materials and Surface Modification Group at EG&G Mound Applied Technologies. In 1956, he received his Bachelor of Science degree in industrial management from Miami Univeristy in Oxford, Ohio. Mr. Schneider has been working as a development chemist in material evaluation and research for the past 20 years, specializing in plastics and adhesive materials.

Table 1 - Test Specification and Batch Results

Formulation	Tensile Strength (M. Pascal)	Compressive Strength (M. Pascal)	Izod Impact (1 cm notch)[a]	Arc Resistance (s)	Heat Distortion (°C)	Flow Rating[b]	Surface Appearances Rating[b]
MIL-M-14G	31.03	110.34	0.30	115	160	6	6
Vendor Supplied[c]	34.48	115.86	0.33	120	165	7	7
Batch 688	38.62	112.41	0.44	123	164	8	8
Batch 694	31.03	122.76	0.65	121.5	167	8	8
Batch 698	46.90	142.76	0.53	121.4	172	8	9
Batch 699	42.07	153.10	0.64	121.5	171	8	9
Batch 018	37.93	116.55	0.41	125	165	8	8
Batch 019	35.17	121.38	0.35	122	164	8	8
Batch R54	47.59	140.69	0.38	119.2	169	8	6

[a] Depth

[b] Rating: 1 = very poor; 6 = acceptable; 10 = excellent.

[c] Typical values.

Table 2 - Fiber Screening Data

Mesh Size	Appearance of Fibers after Screening	% Material Retained on Screen - Various Times		
		10 min	20 min	30 min
+50	Balls	25-40	15-25	13-19
+100	Powder	8-25	5-15	4-9
+200	Fine Powder	20-35	20-27	19-25
-200	Fine Powder	20-25	40-46	52-58

Starting material: Fiber Tech Grade 9174.

Table 3 - L/D Ratio Versus Fiber Mesh Size

Mesh Size	Weight (g)	Volume Occupied (mL)	Bulk Volume	L/D Ratio
+50	10	25	6.25	33
+100	10	18	4.5	24
+200	10	14	3.5	19
-200	10	10	2.5	12.5

FIGURE 5

BULK VOLUME OF VARIOUS L/D FIBERS

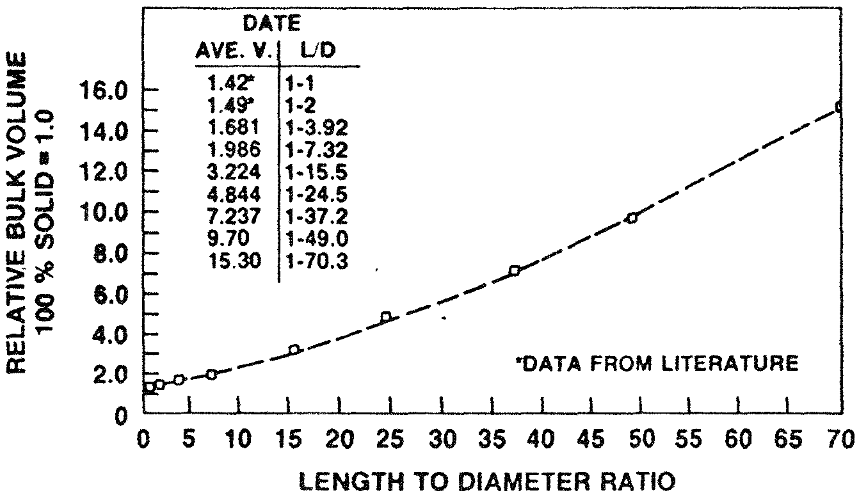


FIGURE 6

DAP BATCH COMPARISON

NORMALIZED AVERAGES

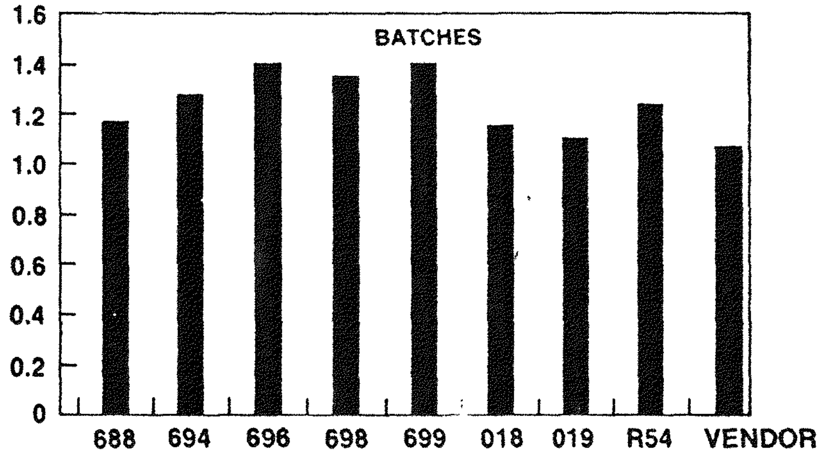
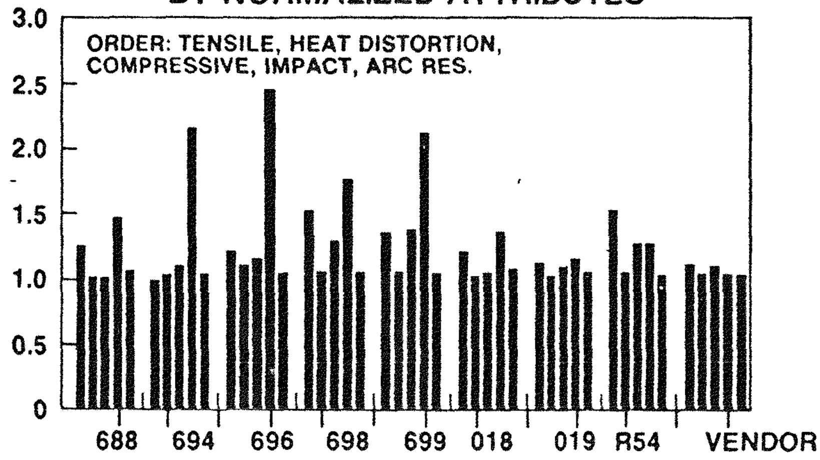
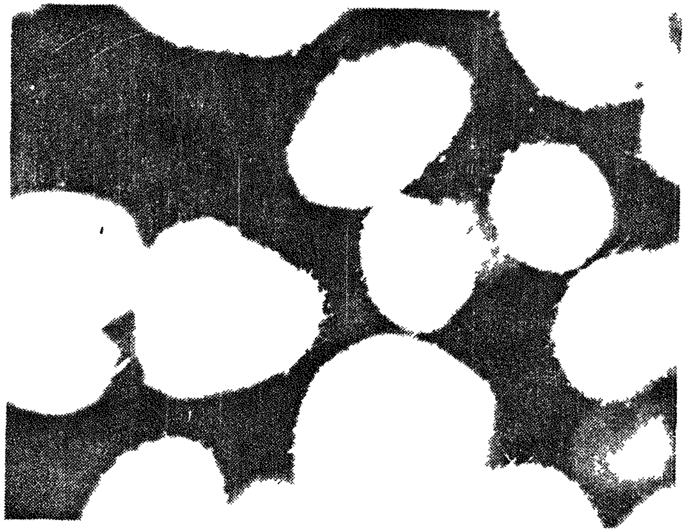


FIGURE 7

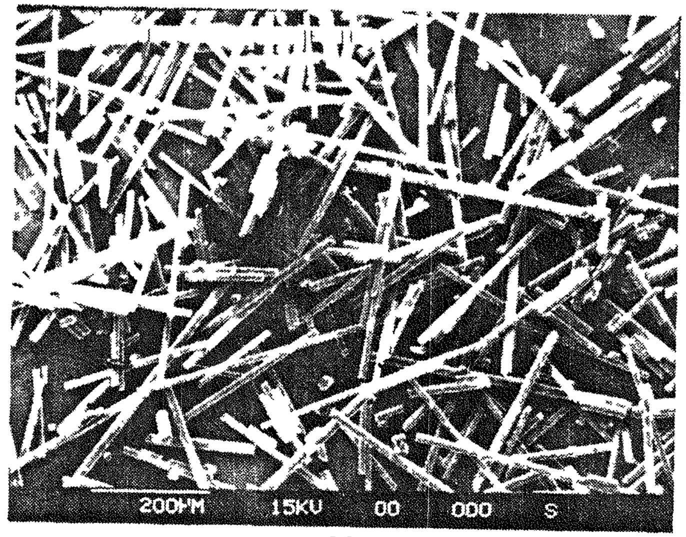
DAP BATCH PERFORMANCE

BY NORMALIZED ATTRIBUTES

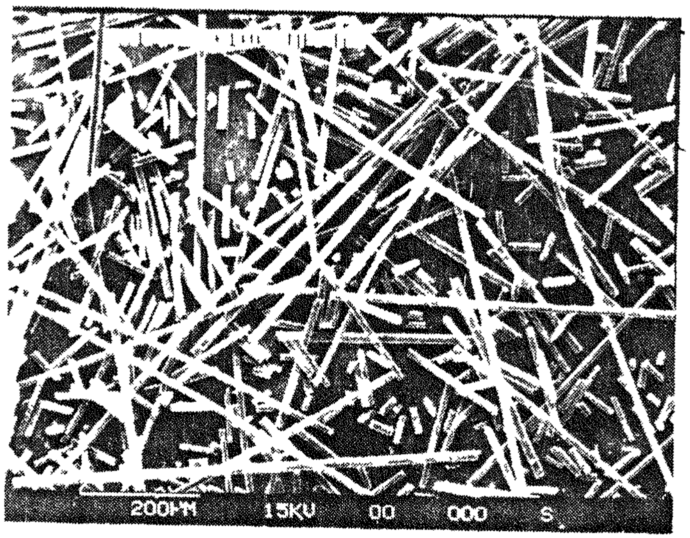




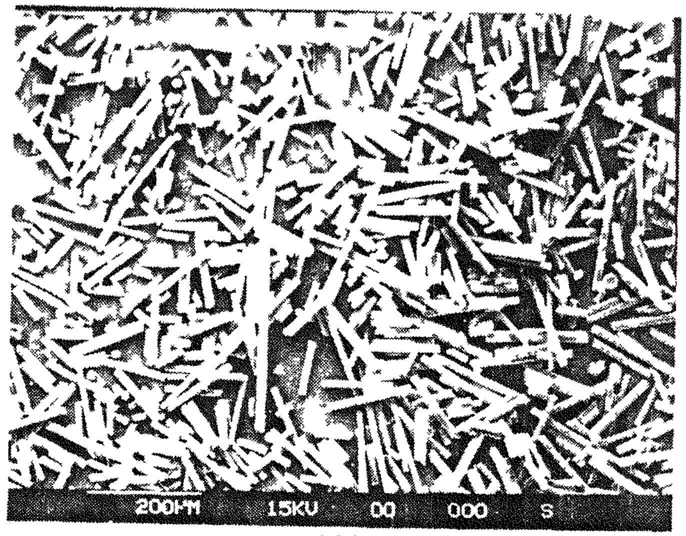
+50



+200



+100



−200

Figures 1–4: Treated figerglass screened through sieves of +50, +100, +200, and −200 mesh.