

Measurement of Adhesion Between Fibers and Fast Curing Elastomer Resin

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SYNOPSIS

A method was developed to measure the adhesion between fibers and fast curing elastomer, in droplet form, using the microbond pull-out method. Samples were fabricated by arranging the fibers as a grid on which elastomer droplets were formed for testing. A droplet sliding test method was developed to investigate the nature of the sites of the droplets on the fiber after displacement of the droplets. Fibers of polyester, aramid, and HMW-polyethylene were tested with resins of polyurethane and natural rubber latex. The fibers had been surface-treated by corona, gamma radiation, or methanol extraction. The shape of the droplets was determined by microscopic measurement. The shear strength of the fiber/matrix bond was tested using a microvise grip in a tensile strength tester. © 1993 John Wiley & Sons, Inc.

BACKGROUND AND THEORY

Elastomer resins and fibers are bonded together in composite structures in which the fibers primarily constitute the load bearing component and the resin, in the form of a matrix structure, holds together the fibers. The load is transferred through the matrix into the composite structure and from fiber to fiber within the structure. The bond strength between fiber and matrix is, therefore, of great importance for the correct function of the composite.

The fiber-matrix bondings can be of either chemical, physical, or mechanical nature, or combinations of these may occur. In the case of the chemical bond, the functional groups of fiber and matrix react with each other to form a covalent linkage. Sometimes an intermediate layer or coupling agent, such as a primer, is used to bond to the fiber and the matrix. In the case of the physical bond, the fiber and matrix are bonded with some physical force, for example, the van der Waals force, or they are interlocked geometrically. In a mechanical bond, the surfaces of the matrix and fiber are locked to

each other by geometrical entanglement, which causes the mechanical linking of fiber and matrix with respect to each other.

Epstein and Shishoo^{1,2} have presented methods to fabricate samples of elastomer composites reinforced with nonwoven fiber structures.

It is important to measure the energy between fiber and matrix and particular attention has been placed on the development of measurement methods for this purpose. Piggot³ reports four main methods. The pull-out and the microtension (microbond) methods are roughly equivalent. These both involve high fiber stresses, which can cause significant Poisson effect of the fiber, pulling its surface away from the matrix, thus reducing the pressure across the interface. The microcompression method requires an FEM analysis for the estimation of the frictional debonding stress τ_d ; the axial force used to debond fiber causes a Poisson expansion, which increases the pressure at the interface. The fragmentation test, in which a single fiber is embedded in polymer and broken into small pieces, is the most realistic from the point of view of the interfacial pressure. The fiber is neither pushed nor pulled directly, so the Poisson effects on the fiber and composite are similar. The fragmentation test produces only one result for the interfacial shear stress, which is the average of the many fragments produced. The test is made

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more powerful by the use of Raman spectral lines to estimate the fiber stress directly from the fiber Young's modulus.

Miller et al.⁴ state that, in order to ascertain the pull-out measurements, the length of the embedded fiber must be small enough to prevent fiber breakage prior to debonding. To overcome the difficulties connected with the fabrication of samples with such small embedding lengths, Miller et al.⁴ developed a new method called the microbond technique. The liquid resin is applied to the fiber under a stereo microscope, using a fine glass applicator (*ca.* 30 μm ϕ). An ellipsoid microdroplet is produced, having only slight menisci at the contact points between the surfaces of the droplet and the fiber (1% of measured embedded length). The embedded fiber lengths, achieved with this process, were calculated to be in the range of 0.007 to 1.0 mm. Materials tested were *E*-glass fibers (ϕ 10–15 μm), Kevlar 49 (ϕ 10–14 μm), and Celion carbon fibers (ϕ 8–10 μm). A matrix of the epoxy system of 4 parts diglycidyl ether of bisphenol-A and 1 part methylene dianiline was used. The measurement of debonding strength was performed in an Instron tensile tester, using a microvise device constructed for this purpose, the plates of which were positioned just above the droplet and close to the fiber so as to produce barely detectable frictional resistance to the fiber. Successful shear debondings were obtained and the nature of the recorded force curves during the trial distinguished proper shear debonding from slipping of the droplet or fiber breakage. Miller et al.⁵ reported fiber diameters, measured with a video micrometer attached to a microscope, using a display with greytone, to determine the location of the fiber boundaries. Gaur and Miller⁶ concluded that the force exerted on the interface in the microbond experiment is predominantly a shearing force. They also concluded that the large distributions of shear strengths, found with the microbond technique, reflect real differences in bond strength attributed to fiber surface heterogeneity. Gaur and Miller⁶ supported their statement with many individual measurements of fiber/matrix systems.

Gaur et al.⁷ developed droplets formed by melting knotted polypropylene fibers on *E*-glass fibers. This technique requires thermoplastic material, available in fiber form, which can be knotted around a fiber and thereafter heated so that the knot melts and forms a droplet around the fiber. This method requires that the knotted polypropylene fiber has a lower melting point than the fiber to be tested.

Brewis and Briggs⁸ reported that the wetting and spreading of a polymer onto a surface is dependent

on the viscosity of the spreading substance, in addition to the surface energies of the substances involved. The degree of wetting was found to be low if the viscosity was high or if the wetting time was short, which is often the case when using reacting or cooling polymers.

For resins with a short pot life and high initial viscosities, none of the above-mentioned methods can be applied, as such. The typical pot life of many two component polyurethane elastomer resins is a few minutes and the initial viscosity is in the vicinity of 20,000 cps at 20°C. Drops of such resin cannot be used with narrow glass applicators or the knotting method. Typical viscosities of epoxy resins are in the range 500 to 1000 cps and pot lives between 15 and 60 min. In order to determine the adhesion of elastomer resins, it was necessary to develop a new method.

EXPERIMENTAL

General

Samples were fabricated by arranging the fibers as a grid, upon which elastomer droplets were formed for testing. A droplet sliding test method was developed to investigate the nature of the sites of the droplets on the fiber after displacement of the droplets. The shape of the droplets was tested by microscopic measurement and the shear strength of fiber/matrix bond was tested using a microvise grip in a tensile strength tester.

Methods for Producing Droplets from Fast Curing High Viscous Resins and from Natural Rubber Latex

During optimal temperature and viscosity conditions, many resins or resin components can be drawn to form a filamentlike resin body. Proper drawing speed, as well as appropriate polymer feeding to the drawing instruments, are important factors that affect suitable formation of such resin fibers.

Our studies have shown that if such an uncured resin filament hits a textile fiber transversally, part of the resin fiber adheres to the textile fiber and forms a droplet around it. If the resin filament is placed across a grid of parallel textile fibers, a particular effect has been noted. The resin filament shrinks and, in the process of shrinking, filament breaking occurs. This breaking mechanism of resin filaments results in the formation of resin droplets at each crossover point along the textile fibers. This process is illustrated in Figure 1.

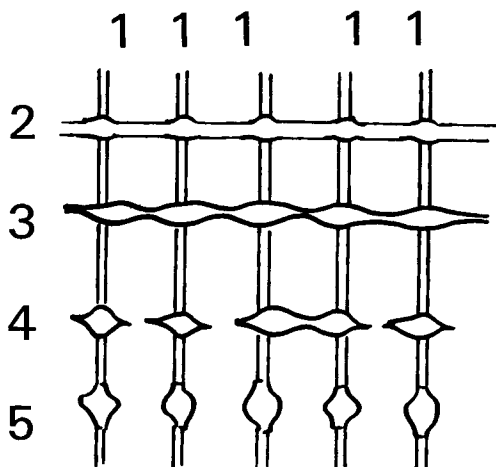


Figure 1 Droplet formation: (1) textile fibers, (2) resin filament placed on grid of textile fibers, (3) resin filament in the process of shrinking, (4) droplets in the process of formation, and (5) elastomer droplets on fibers.

After preliminary trials involving stationary textile fibers, mounted singularly or as grids, a method using a moving grid of textile fibers was developed. Individual textile fibers were mounted manually by suspending them straight between two wheels and attaching each fiber end to double-sided tape on each wheel, respectively, to form fiber grids on the wheels. For crimped or thin fibers, magnifying lenses were used to aid in the mounting. The distance between the wheels in the assembly was determined by the length of the fibers, so as to allow good fastening and as large a free length of fiber as possible. Typically, the wheel assembly had up to seven wheel pairs on a shaft, connected to a mixer and a supporting bearing. A wheel diameter of 4 cm and a rotational velocity between 120 and 400 rpm was found to be the most practical. This gave perimeter velocities of between 14 and 48 meters per minute. The actual velocity for each experiment was selected depending on the viscosity and fiber-forming ability of the resin. The number of fibers in one grid assembly varied between 46 and 60 and the average distance between the fibers in the grid varied between 2 and 3 mm. The resin was then ejected, at a proper rate, from a syringe and was allowed to form a thin resin filament with gravity. The emerging filament was then brought into contact with the rotating fiber grid, whereby the fiber was increasingly drawn and its continuation was controlled by feeding more resin from the syringe. Figure 2 shows the process for producing droplets and Figure 3 shows a typical fiber grid with droplets. After formation, the grid was left to rotate at about 100 rpm, driven by

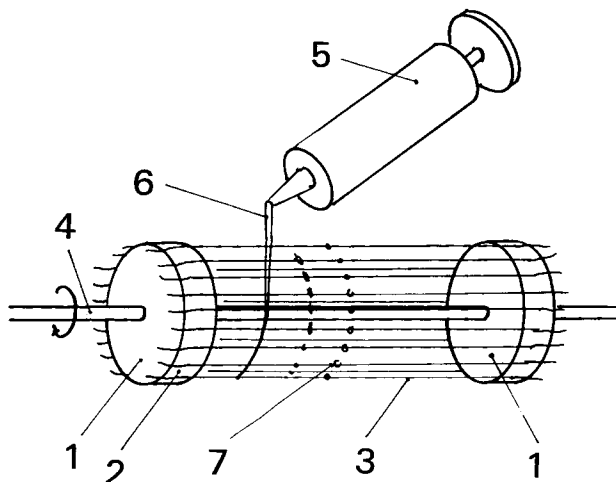


Figure 2 Process for producing droplets: (1) wheels, (2) double sided tape, (3) fiber, (4) shaft, (5) syringe, (6) resin filament, and (7) droplet on fiber.

stirrer, until the resin had cured enough to avoid distortion of the droplets due to the gravitational force. The droplets were then allowed to cure overnight, followed by removal of the grid of fibers from the wheel assembly by peeling off the tape with the fibers directly onto a black cardboard surface, as shown in Figure 4.

Polyurethane was primarily used as the material for droplets. For comparison purposes, polyester and epoxy resins were used in trials on a limited scale, using the method described above.

Measurement of the Adhesion

Materials

Fibers. The fibers used were of three different generic types, *viz.* polyester fibers having a fineness of

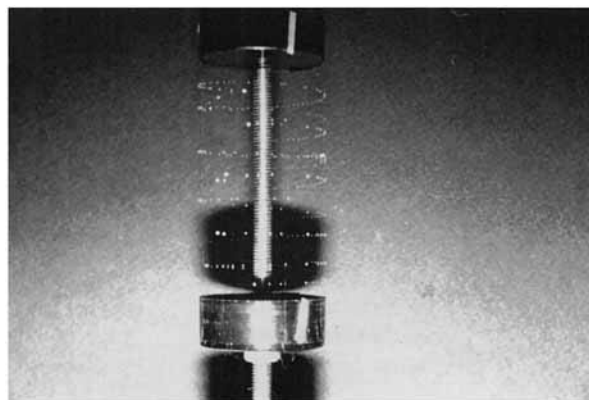


Figure 3 Typical fiber grid with droplets on fibers.

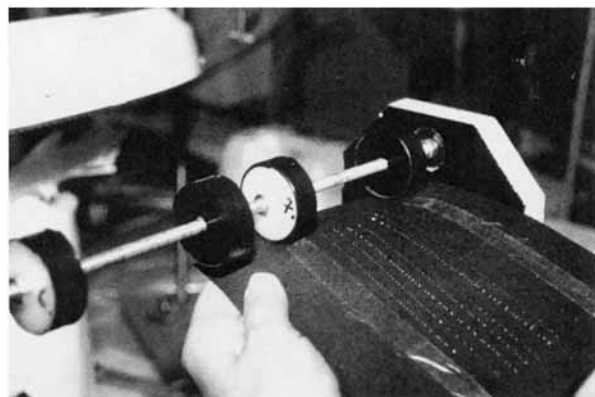


Figure 4 Removal of fiber grid with droplets from wheels.

0.7 dtex, a tenacity of 36.2 cN/tex, and an elongation at break of 43.6%. Aramid and gel spun HMW-polyethylene fibers, with a fineness of 1.7 and 1.1 dtex, respectively, and tenacities of 156 and 214 cN/tex, respectively, and elongations of 4 to 6%, were also used. They were given one or several of the following surface treatments before the formation of elastomer droplets:

1. Methanol extraction to remove finishing agents.
2. Cured epoxyde coating to improve adhesion to rubber.
3. Corona treatment.
4. Gamma-radiation.

In order to compare, untreated fibers were also used.

The methanol extraction was performed using a Soxhlet extractor for six extraction cycles. The Corona treatment was performed by the fiber manufacturer. For gamma-radiation, samples of fibers were radiated for 66 h in a ^{60}Co -source, so that the calculated radiation dose corresponded to 6 Mrad. The fibers tested are reported in Table I.

Matrix Polymers. The elastomeric matrix polymer consisted of a system (Baytech from Bayer Ag), in which the polyol was a polyether compound, containing small amounts of tertiary aliphatic amine and a primary aromatic diamine, with activator added. The compound's viscosity was measured to 3000 cP at 20°C. The isocyanate was a polyether-TDI prepolymer with isocyanate groups. Its viscosity was measured to 20,000 cP at 20°C, 3000 cP at 40°C,

Table I Fiber Specimens Used in the Experiments

Specimen	Fiber Type	Polymer Type	Treatment
Aramid Fibers			
A1	Twaron Filament	Aramid	None
A2	Twaron Filament	Aramid	Methanol Extracted
A3	Twaron Filament	Aramid	Epoxyde Treatment
A4	Twaron Filament	Aramid	Epoxyde Treatment, Methanol Extracted
A5	Twaron Filament	Aramid	Epoxyde Treatment, Gamma Radiated
A6	Twaron Filament	Aramid	Epoxyde Treatment, Methanol Extracted, Gamma Radiated
Polyester Fibers			
P1	Diolen Micro 100 t/144, Fil.	PES	None
P2	Diolen Micro 100 t/144, Fil.	PES	Methanol Extracted
P3	Diolen Micro 100 t/144, Fil.	PES	Gamma Radiated
P4	Diolen Micro 100 t/144, Fil.	PES	Methanol Extracted, Gamma Radiated
HP-Polyethylene Fibers			
E1	Dyneema, Fil.	Polyethylene	None
E2	Dyneema, Fil.	Polyethylene	Methanol Extracted
E3	Dyneema, Fil.	Polyethylene	Gamma Radiated
E4	Dyneema, Fil.	Polyethylene	Methanol Extracted, Gamma Radiated
E5	Dyneema corona, Fil.	Polyethylene	Corona Treatment
E6	Dyneema corona, Fil.	Polyethylene	Corona Treatment, Methanol Extracted
E7	Dyneema corona, Fil.	Polyethylene	Corona Treatment, Gamma Radiation
E8	Dyneema corona, Fil.	Polyethylene	Corona Treatment, Methanol Extracted, Gamma Radiation

and 800 cps at 60°C. The advantage in S-RIM processing, as compared to many other elastomers, is low viscosity; the disadvantage of the compounds is short pot life (max. ca. 2 min). As a polyester matrix, a system of resin G300TPA, from Neste Oy, with methylethylketen peroxide (Katalysator No. 1 from Nopco) was used and as an epoxy matrix, a system of GY1823 and HY830 from Ciba Geigy was used.

The natural rubber latex had a rubber content of ca. 60% dry rubber as dispersed in water. Six and one-third parts of vulcanizer, based on 100 parts dry rubber, were added. The vulcanizer consisted of 57% (weight) ZnO, 24% sulfur, 16% zinc mercaptotiazol, and 3% diphenyl guanidine.

Fabrication Process for Fiber Samples with Resin Droplets

The components of the resin, one part polyol to one and one half parts isocyanate, were mixed in a 20 mL beaker with a propeller mixer for 2 min and the mixture was sucked into a syringe. Afterwards the grid assembly was set in rotation and the droplets on fiber substrate were produced and cured.

In order to investigate the influence of resin aging, with respect to droplet formation and adhesion, groups consisting of 5.5 dtex methanol extracted polyester, 1.7 dtex methanol extracted aramid fibers, and 1.7 dtex unextracted adhesion-treated aramid fiber were mounted with equal interfiber distances on four pairs of identical wheel pairs, fitted on a common shaft.

In order to define the influence of the interfiber distance on the dimensions of the droplets, polyester fibers were mounted on the wheels in groups of five fibers, having interfiber distances of 0.5, 1.0, 1.5, 3.0, 5.0, and 8.0 mm, respectively, within the respective groups. The tests were conducted with resin of three different aging times, respectively, viz. 60, 120, and 180 seconds. The diameter and length of each droplet emerging from each resin fiber, from the experiments with different interfiber distances, were measured. The diameter of the droplets on the innermost fibers of each group was measured, using the method described in the "Testing Procedures" section (see Fig. 5). Only droplets generated from resin fibers that contacted fiber groups, representing four or more distance groups, were considered to be representative.

To compare with other elastomers, droplets of natural rubber were produced by spraying latex, in the form of fine droplets, onto a grid of fibers fastened in a frame. Both adhesion-treated as well as methanol extracted nontreated aramid fibers were

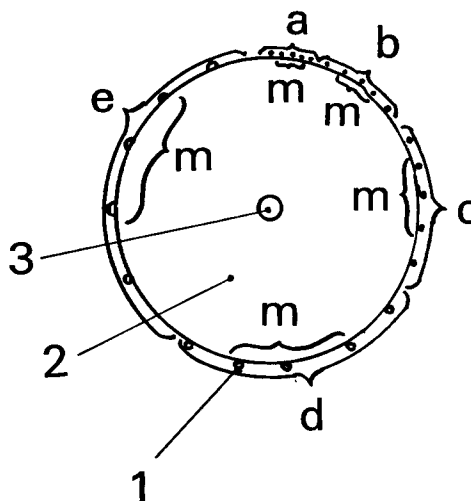


Figure 5 Arrangement of fibers for studying the influence of interfiber distance: (1) fiber with droplet, (2) wheel, (3) shaft, (a-e) groups of fibers having particular interfiber distances, (m) fibers on which droplets were measured.

used. The droplets were left to dry at room temperature overnight, whereafter the rubber was vulcanized by maintaining the droplet covered fibers in an oven at 105°C for 1 h.

In order to assess the fineness of the resin filaments, release paper was mounted instead of fibers on the pairs of wheels, whereafter resin filaments were formed on the release paper in the same manner as when droplets were formed on the fibers.

Testing Procedures

Each droplet was individualized by numbering the individual fibers and the individual rows of droplets, while the fibers were attached to the blackboard used in connection with the removal of fibers from the wheels. The numbers were marked on the blackboard with a white pencil while viewing fibers and droplets under the microscope.

The plates of black cardboard, with the adhered grid of fibers and droplets, were photographed in a 1 : 1 scale, using a xerographic copying process.

The dimensions of the droplets obtained were measured using a microscope connected to a video-camera and monitor (Wild MSA stereo microscope with Panasonic Color CCTV camera and Panasonic BT-M 1400 PSIV monitor). The analysis was made with the fibers attached to the blackboard. The length of the bonding zone between fiber and droplet, as well as the diameter of the droplet perpendicularly to the fiber direction, were measured on the monitor

using a ruler, which was calibrated against a scale under the microscope. The contact angle between the fiber surface and the surface of the droplet was also measured on two sites, using a grade scale on the monitor, as shown in Figure 6. The average of the two measurements was taken as a representative value for the contact angle. The diameter of the control samples of the textile fibers was also measured using the microscope.

Scanning electron microphotographs of droplets and fibers were made using a Jeol JSM-T100 microscope after sputtering the samples in a Balzers SCD 050 Sputter Coater. The samples were fastened on metal mounts with a groove to allow the droplets to hang freely on the fibers. Droplets that were tested for shear strength, as well as untested droplets, underwent SEM microscopy. The droplets were investigated and the fibers were scanned to find polymer traces on the fiber surface on sites in which the droplets had been situated before shear strength testing. Photographs of the cross section of the droplets with transversing fibers were made after cleaving the droplet along the direction of the fiber with a surgeon's knife.

The tenacity and elongation at break of fibers, prior to the application of elastomer droplets, were tested on a Lenzing Vibroskop and Vibrodyn tester using 25 fibers of each fiber type tested.

The diameter of the fibers was calculated from eq. (1) and the shearing stress was calculated from eq. (2).

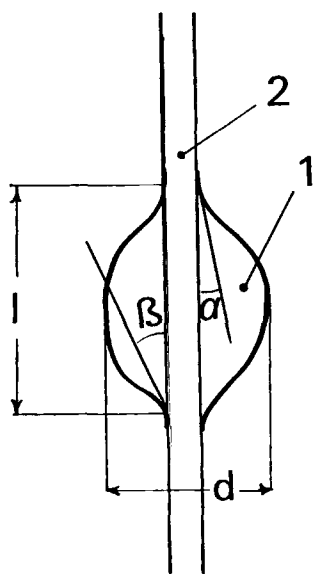


Figure 6 Dimensions measured on droplet: (1) droplet, (2) fiber, (l) length of bonding zone (droplet length), (d) diameter of drop, and (α , β) contact angles.

$$d_f = \left(\frac{4 \times f}{\pi \times 10^4 \times \rho} \right)^{1/2} \quad (1)$$

$$S = \frac{F}{\pi \times d_f \times l_d} \quad (2)$$

where (d_f) diameter of textile fiber, (f) fineness of textile fiber, (ρ) specific weight of textile fiber, (S) shearing stress, (F) shearing force, and (l_d) length of bonding zone.

The shear strength of the fiber/matrix bond, hereafter called the shear bond strength, was measured according to the microbond pull-out method, using a tensile strength tester (Alwetron Typ 14-1) with a droplet grip microvise of the type described by Miller et al.⁴ Before placing the droplet into the vise, the fiber was pretensioned by attaching a 50 mg weight to its lower end. The vise was attached to the lower jaw of the tester. The fiber specimens were pulled out of the microdroplets at a rate of 10 mm per min. The number of droplets tested for each fiber type was between 8 and 39.

A droplet sliding test, using the tensile strength tester and the microvise, was performed for a number of fibers on which several droplets had been produced. The droplets were pulled one by one, starting from the lowest, along the fiber, finishing the pulling close to the lower end of the fiber, stopping the pulling when it hit the previously pulled droplet. The frictional force was recorded for each droplet during the pulling operation. Each droplet thus passed the sites on the fiber of the previous droplets (see Fig. 7). The curves for the individual drops were arranged over each other on the graph paper, so that the point representing the stop in each curve was placed on the y -axis of the graph. A picture of the fiber before testing with the droplets on their original sites was placed below the displacement- (x -) axis of the graph. The fiber was pictured on the same scale as the displacement-axis.

RESULTS

Droplet Fabrication

Large numbers of matrix resin droplets on fibers could be produced rapidly from Baytech polyurethane elastomer and from Neste G300TPA polyester resin, after the right conditions for polymer filament forming were obtained. Larger rotational velocity of the wheels yielded finer filaments and smaller droplets. The GY1823/HY830 system epoxy resin used could not be formed into polymer filament for droplet production.

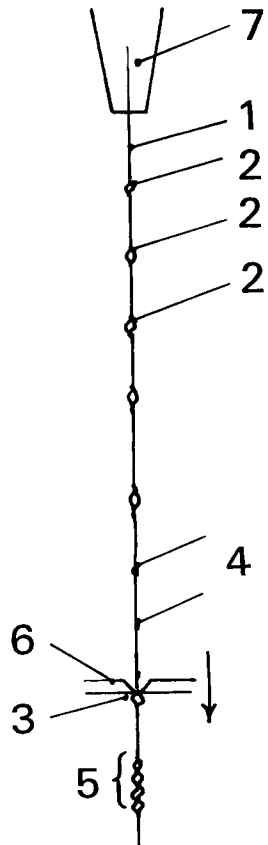


Figure 7 Droplet sliding test: (1) fiber, (2) droplets on fiber, (3) droplet being pulled, (4) sites on fiber from where droplets have been pulled, (5) droplets pulled towards lower end of fiber, (6) microvise, and (7) clamp holding fiber.

The manual mounting of the fibers proved to be a tedious and time-consuming process, which put strain on the eyes of the operator. The individualization of the droplets by marking made it possible to use many droplets on the same fiber as test specimens for microbond testing, which facilitated the test operation.

Microbond Pull-Out Tests

The diameters of the fibers were calculated, using eq. (1), to 0.008 mm for Diolen Micro polyester, 0.0122 mm for Twaron aramid, and 0.0120 for Dyneema polyethylene fibers.

The stress-strain curves of the shear bond strength test exhibited a steep rise in force, ending in abrupt breakage. Only in few cases a stepwise rise occurred, showing primarily one step only. The tests involving 0.7 dtex polyester fiber showed larger dis-

placement than tests with the other fiber types. Figure 8 shows a typical stress-strain curve.

The standard deviation values for the microbond pull-out test results were high for all cases tested. Notwithstanding, some trends were visible from the results.

The tests clearly indicate that the epoxy-treated Twaron aramid filament fibers retain better adhesion to polyurethane elastomer than corresponding nontreated fibers or any other type of fiber tested. The tests results are shown in Table II. The corona and gamma-radiation treated Dyneema HP-polyethylene fibers had clearly better adhesion than the other Dyneema types. The Twaron crimped staple fibers, the Diolene Micro polyester fibers, and the corona and gamma-radiation treated Dyneema HP-polyethylene fibers exhibited test values with similar magnitude. The test results for gamma-radiated fibers are shown in Table III.

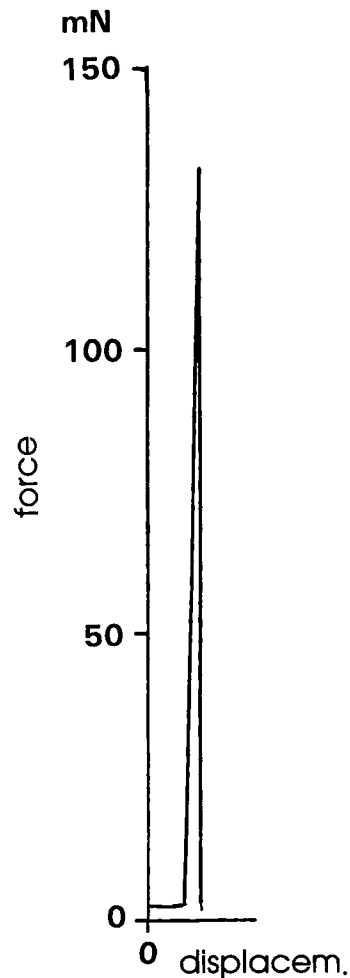


Figure 8 Typical stress-displacement curve from shear strength test of fiber/matrix bond.

Table II Influence of Fiber Surface Treatment on Shear Bond Strength

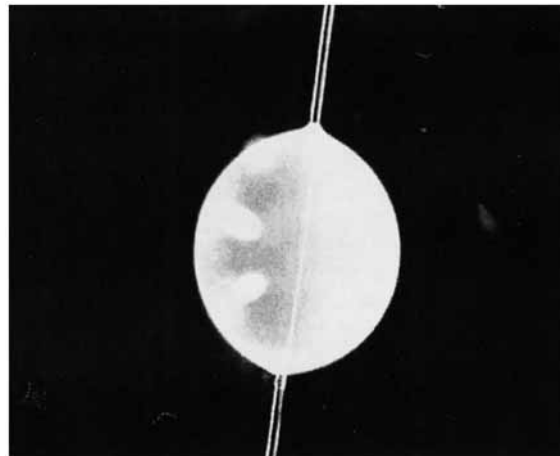
Specimen	Number of Droplets	Shear Stress (mN/mm ²)	Standard Deviation
Aramid Fibers			
A1	21	3430	774
A3	20	15,102	6200
A4	20	9679	4212
A6	17	7073	1692
Polyester Fibers			
P1	22	2850	905
P2	24	2891	932
P3	16	2533	1091
P4	18	2483	893
HP-Polyethylene Fibers, Noncorona			
E1	35	612	310
E2	11	469	229
E4	21	3787	1547
HP-Polyethylene Fibers, Corona			
E5	25	3231	1139
E6	15	1198	885
E8	19	2424	1438

Droplet Form

The form of the droplets was regular for all types of fibers, the ratio of length to diameter, here called symmetry, was 1.03 to 1.34, and the correlation length to diameter, within each fiber type, was high. The measurement of the contact angle between the droplet and the fiber surface proved difficult and no

Table III Changes in Shear Bond Strength Due to the Effect of Gamma Radiation on Fibers

Specimen	Number of Droplets	Shear Stress (mN/mm ²)	S.D.
Aramid Fibers			
A3	20	15,102	6200
A5	21	8213	3593
Polyester Fibers			
P1	22	2850	905
P3	16	2533	1091
HP-Polyethylene Fibers, Noncorona			
E1	35	612	310
E3	13	616	183
HP-Polyethylene Fibers, Corona			
E5	25	3231	1139
E7	16	1813	1552

**Figure 9** Microphotograph of typical droplet.

greater precision could be achieved. A microphotograph of a typical droplet, formed around a fiber, is shown in Figure 9.

The tests with a resin of a different age exhibited a decreasing capability for droplet formation, especially with resins above 420 s of age; the resin fibers did not break between the textile fibers in the grid.

There was positive correlation between droplet length and interfiber distance for resin up to 120 s in age; above that age the correlation decreased. The results from the measurements are shown in Table IV. The contact angle measurements showed an increase in contact angle from 30° to 34° after corona treatment of Dyneema HP polyethylene fibers and

Table IV Influence of Interfiber Distance on Droplet Formation

Resin Age	Interfiber Distance (mm)	Droplet Length (mm)	S.D.
60 s	0.5	0.20	0.00
	1	0.33	0.08
	1.5	0.34	0.07
	3	0.46	0.15
	5	0.43	0.18
180 s	8	0.63	0.21
	0.5	0.26	0.16
	1	0.28	0.09
	1.5	0.37	0.22
	3	0.36	0.17
	5	0.47	0.07
	8	0.49	0.11

an increase to 36° and 40° after methanol extraction and after gamma-radiation, respectively, of Dyneema HP polyethylene fibers.

Droplet Sliding Test

In the droplet sliding test experiments, the friction of the droplet against the fiber increased when the sliding droplet passed over the site of a previous droplet. This effect was represented by a number of humps in the stress-strain curve. The degree of friction at a particular droplet site decreased in proportion to the number of droplets that had been

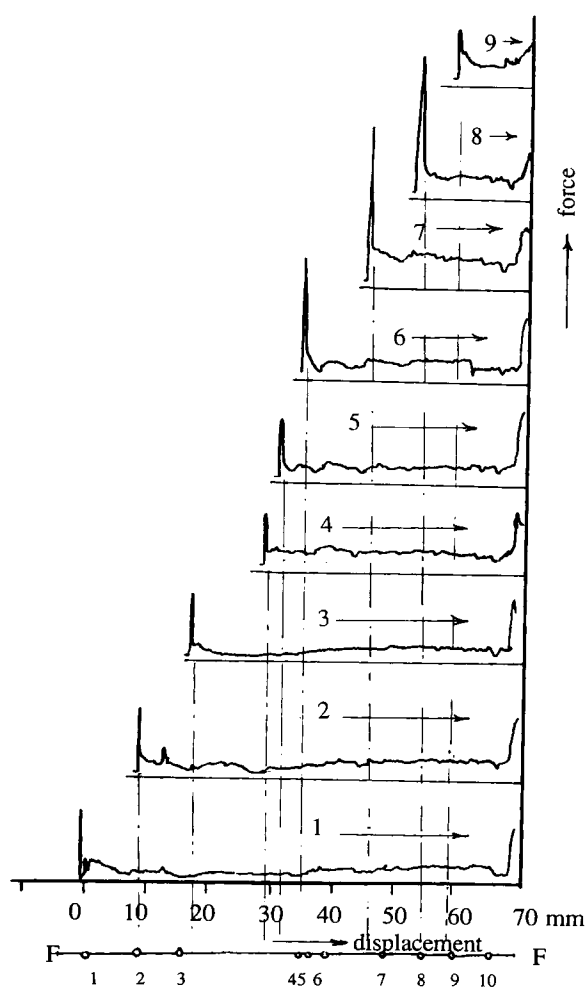


Figure 10 Diagram of set of stress-strain curves from droplet sliding test. F-F represents the fiber with rings, indicating droplets on their sites on the fiber before testing, drawn in the same scale as the displacement- (x -) axis in the diagram; numbers beside the arrows represent the droplet tested; arrows indicate the direction of pulling; the droplets were pulled in the order: 10, 9, 8, 7, 6, 5, 4, 3, 2, 1 (curve of 10 not shown).

Table V Influence of Matrix Polymer Type on Shear Bond Strength

Specimen	Number of Droplets	Shear Stress (mN/mm ²)	S.D.
Polyurethane Matrix			
A3	20	15,102	6200
A2	39	2564	681
Rubber Latex Elastomer Matrix			
A3	21	1970	1433
A2	17	1455	499

pulled over that particular site. A typical set of stress-displacement curves for individual droplets is shown in Figure 10. The curves were placed above each other so that the curve, representing the lowest droplet on the fiber, is situated at the top of the figure and the curves of the following droplets succeeding downwards. The points closest to the vertical (y -) axis in the graph represented the end of the sliding travel, that is, the place at which the droplet hit the previous droplet. The curves showed repetitiveness with maxima corresponding with the droplet sites along the fiber. A decrease of frictional force was also noted at the individual droplet sites after an increased number of passages by succeeding droplets.

Natural Rubber Latex Elastomer Tests

The droplets in the experiments involving natural rubber latex were of spherical shape, with a form similar to the polyurethane droplets. In addition, the contact angles had values that were similar to those seen in the polyurethane droplets. The surface was less glossy than that of the polyurethane droplets. The microbond pull-out shear stress values were lower than the corresponding ones involving polyurethane elastomer on corresponding fibers. Particularly, the shear bond strength for epoxyde-treated aramid was only a fraction of that of polyurethane elastomer and approximated the value of that for latex droplets on extracted untreated aramid fiber. The results are presented in Table V.

SEM Photographs

The SEM photographs of the debonded fiber/droplet interface showed fibrillation for some cases of aramid fibers (Fig. 11). Fibrillation, where part of the fibrilles seemed to have moved with the droplet, was noted particularly for fibers that exhibited

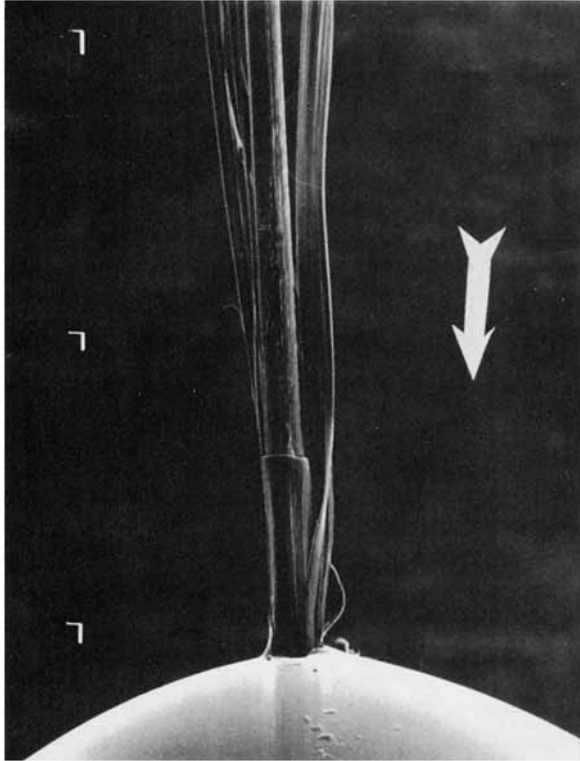


Figure 11 SEM-photograph showing fibrillated aramid fiber after shear-bond-strength test. Arrow shows direction of pull.



Figure 13 SEM-photograph of half of cleaved droplet, with the fiber visible. The other half of the droplet is shown in Figure 12.



Figure 12 SEM-photograph of half of cleaved droplet with fiber; the trace of the fiber in the droplet is visible.

higher shear bond strength values. Other fiber types tested did not show any fibrillation.

Figures 12 and 13 show a pair of halves from the one and same cleaved droplet. The trace of the fiber in the droplet (Fig. 12) showed a smooth surface and the corresponding fiber surface is practically clean (Fig. 13). In some cases, remnants of polyurethane elastomer were found on the fiber surface on sites where the droplet was situated before shear strength testing; latex elastomer remnants occurred much more frequently. No traces of damage by the jaws of the TRI-type vise, used in the shear stress tests, could be seen on the droplets.

The contact angles, seen on some of the SEM photographs, appear to be smaller than those measured in the microscope. The photographs of droplets from a polymer of a different age showed an increase in the contact angle for increasing age (Figs. 14–16).

DISCUSSION

The spreading behavior of the polyurethane resin on the fibers is apparently dominated, to a relatively

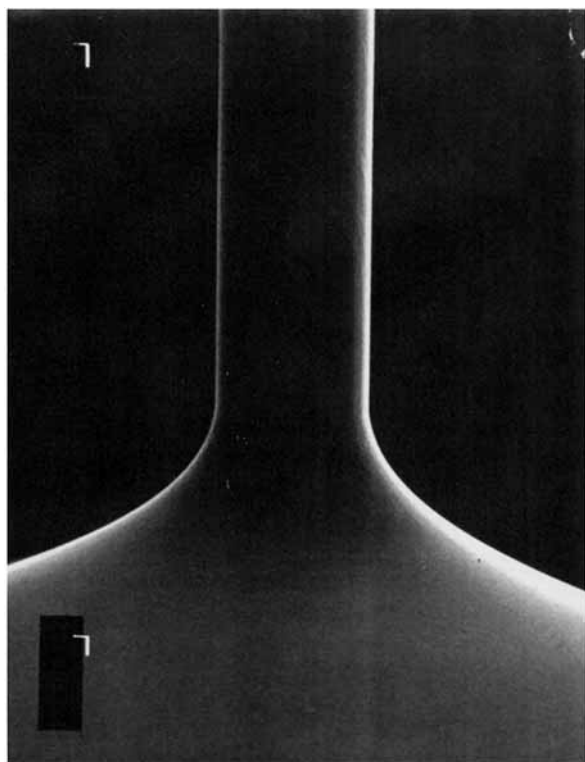


Figure 14 SEM-photograph of contact angle between elastomer and fiber, age of elastomer 2 s.

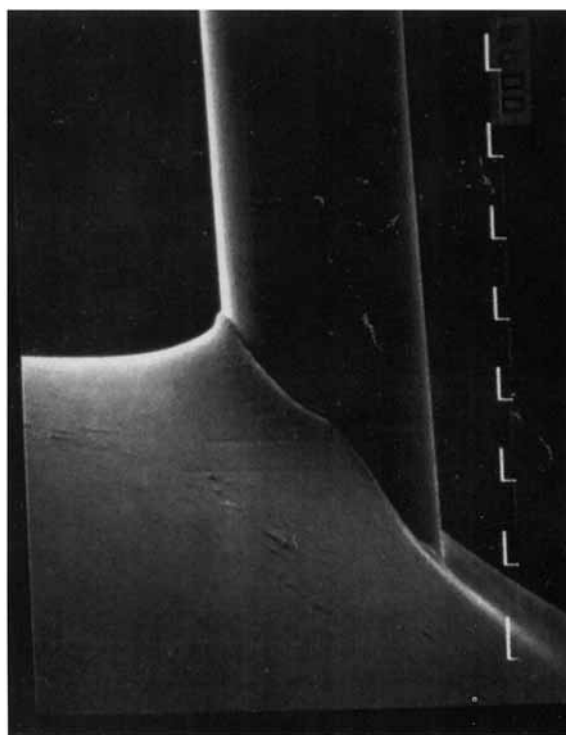


Figure 16 SEM-photograph of contact angle between elastomer and fiber, age of elastomer 10 min.

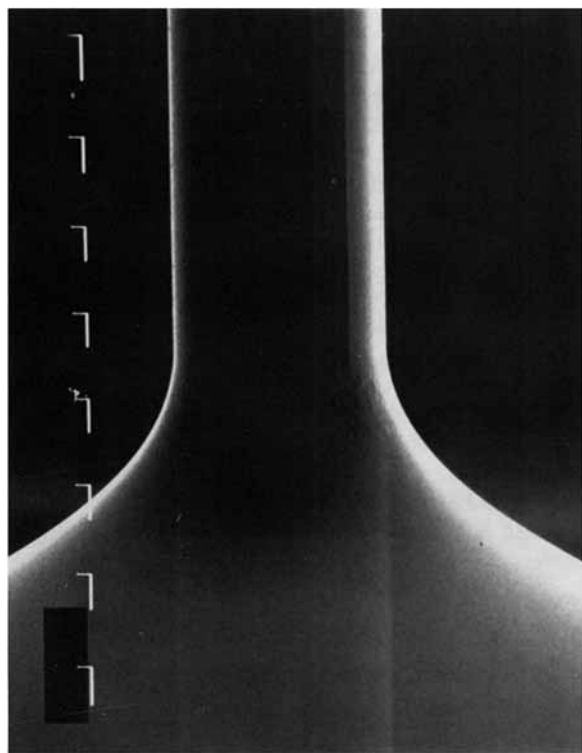


Figure 15 SEM-photograph of contact angle between elastomer and fiber, age of elastomer 2 min.

large extent, by the viscosity of the resin. The inability to produce droplets from resins older than a certain age is most likely due to the decreased ability of the resin to flow within the resin filament, because the resin viscosity has increased with age due to increased polymerization. Therefore, the filaments of older resin cannot break between the textile fibers in the grid. Similar behavior could be noted for the polyester resin. Droplets could not be formed from the epoxy resin because of its inability to form polymer filamentlike bodies, which is probably caused by its low viscosity.

The positive correlation between droplet diameter and interfiber distance during droplet fabrication indicates that the longer the interfiber distance, the bigger the length of resin filament that is allotted for each droplet. In addition, the fineness of the resin influences the droplet size. The regular form of the droplets, and the similarity of length and diameter, indicate that the broken filament contracts to approximately spherical form, due to high surface tension of the resin.

The measurement of the contact angle in the microscope proved inexact, due to difficulty in detecting the borderline between the matrix and the fiber surface. The SEM photographs indicate that the contact angles may be smaller than those seen in the

stereo microscope. However, the contact angles, measured in the stereo microscope, for Dyneema HP polyethylene fibers indicate that corona treatment, methanol extraction, and gamma radiation increase the contact angle.

The shape of the stress–displacement curves indicate that the debonding occurs abruptly, so that the droplet debonds practically at once over the whole contact surface. The somewhat larger displacement, noted for the 0.7 dtex polyester fiber, is most likely due to the higher elongation ability of this fiber type, noted in the tenacity–elongation test performed on the fibers.

The large standard deviation values in our tests may be due to a relatively low number of specimens, although an increased number of droplets did not always improve the deviation values. The results indicate that this test method can detect differences in microbond strength between fibers, with different surface treatments, if the effect of the treatment is strong. This test method can also distinguish between microbond strength values of matrix elastomers of widely differing polymer characters and with different application methods.

The influence of cohesive failures within the matrix and fiber could not be evaluated, because no analysis on the strength of the elastomer materials or the interlaminar strengths of the fibers were made in this investigation.

The droplet sliding test, where the droplets were being pulled over sites of previous droplets, revealed an increase of friction at the sites, which can be regarded as residual stress. This indicates that residuals of the separated droplets remain on the fiber surface.

CONCLUSIONS

We have devised a method to produce rapidly large amounts of droplets to be used as specimens for microbond pull-out testing, permitting analysis of many droplets on one fiber. This work was undertaken because of the shortcomings in the existing droplet formation methods, when used to produce small droplets from viscous fast-curing elastomer polymers. Our investigations have indicated that surface treatment of the fibers is important for the

adhesion of polyurethane elastomers to fibers. Debonding can occur either in the elastomer layer or in the boundary between the fiber and elastomer, depending on the fiber type, matrix type, and fiber treatment. Fibrillation of fibers may also occur in connection with the microbond pull-out test.

The droplet formation was uniform and the dimensions of the droplets could be controlled using the developed method. The aging of the elastomer has an effect on the contact angle between the elastomer and the fiber and also on the formation of the droplets. The new method has been compared with another method of producing elastomer droplets on fibers, *viz.* using elastomer in latex form. It is important in future work to include studies of the influence of cohesive failures within the fiber and matrix in connection with microbond pull-out tests.

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