Studies of the Effect of Fiber Surface and Matrix Rheological Properties on Nonwoven Reinforced Elastomer Composites

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SYNOPSIS

The influence of fiber type and fiber-surface properties on matrix flow behavior was investigated using structural reaction injection-molding (SRIM). The influence of fiber type, fiber-surface properties, and matrix type on strength properties in elastomeric composites reinforced with nonwoven fibrous structures was investigated using tensile tests on elastomer composite samples from SRIM and latex coagulation (LC) fabrication methods and the microbond strength method on individual fibers. The fibers used were PET, LLDPE, and p-aramid. Fibers were treated with epoxy, styrene, and isocyanate derivatives, which make the surface chemically reactive. Treatments were also made with NaOH and a copolymer of polyester and polyol ether, causing a change in the fiber surface energy. The matrix types were polyurethane elastomer and natural rubber. The results show that the surface treatments which produced a change in the surface energy influenced the flow rate of the matrix polymer during the composite fabrication process. The treatments resulted in chemically reactive fiber surfaces which improved the fiber–matrix bond strength without affecting the Young's modulus of the composite material. Good correlation was found between bond strength and surface energy including the dispersive component of surface energy in the case of polyurethane elastomer and surface-modified PET fibers. The age of the polyurethane matrix has a marked influence on the bond strength. The fiber volume fraction in composites has a strong influence on the Young's modulus of the elastomer composite. © 1995 John Wiley & Sons, Inc.

BACKGROUND

The structural reaction injection-molding (SRIM) technique in the fabrication of composites containing an elastomeric matrix and a three-dimensional fibrous reinforcement structure has thus far attracted little scientific attention as reflected by the scarce data in the literature. The authors have earlier described methods to produce elastomeric composites with three-dimensional fibrous reinforcements using both SRIM[1] and latex coagulation (LC)[2] techniques. The role of various fabrication parameters for these types of composites was reported earlier.[3]

Very little information exists in the literature concerning the influence of surface properties of the fibers and matrix on the fabrication processes and on the mechanical properties of such composites. Data about the influence of surface properties on fiber–matrix bond strength and data on the strength properties of elastomer composites with three-dimensional fibrous reinforcement is also scarce.

THEORETICAL CONSIDERATIONS REGARDING FIBER–MATRIX BONDING AND POLYMER FLOW

Bonding, Wetting, and Adhesion Phenomena in Composite Materials

The bond formations between fiber and matrix in an interface are of three main types, i.e., chemical bonding, bonding involving van der Waals forces,
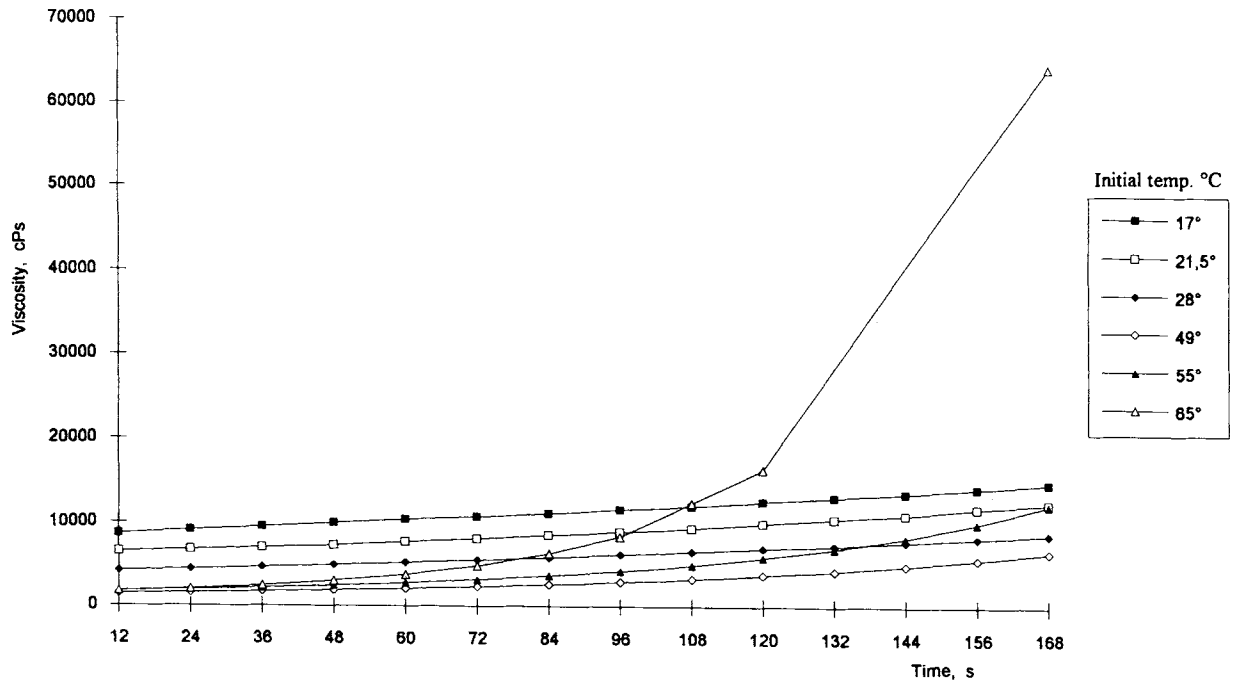
Figure 1   The rate of change of viscosity of polyurethane matrix polymer measured at different initial temperatures of polyol and isocyanate.

and mechanical bonding. The surface energy can be divided into two components: the dispersive or non-polar component and the polar component. They relate to the corresponding components of the van der Waal's force between molecules: The dispersion force depends on the electron frequency of the molecule, and the polar force depends on the dipole, induction, and hydrogen-bonding interactions.

The dispersive and polar components of the surface energy of a solid surface, such as a fiber, may be calculated from contact angle measurements us-

ing two liquids that have different ratios between polar and dispersive components; the surface energies of both liquids must be known. Using the harmonic-mean equation in the Young's equation, one obtains an equation-pair from which the polar and dispersive components for a solid surface can be solved, based on values from contact angle measurements on two liquids with surface energies of the kind described above.[4]

The effect on adhesive bond strength by the wettability of a liquid, e.g., an adhesive, can be expressed as

Table I   Surface Energy of Surface Fibers and Polyurethane Matrix

Fiber	Treatment	Surface Energy, Solid (Harmonic-Mean Method) ($\times 10^{-3}$ N/m)		
		Dispersive	Polar	Total
p-Aramid	None	27.6	24.0	51.6
p-Aramid	Epoxide	26.7	24.9	51.6
PET	None	38.2	10.3	48.5
PET	NaOH	18.9	10.7	29.5
PET	Fluorocarbon	22.1	8.2	30.3
PET	PET–PG–E	22.5	20.7	43.2
LLDPE	None	27.6	12.1	39.7
PU matrix		24.3	9.6	33.9

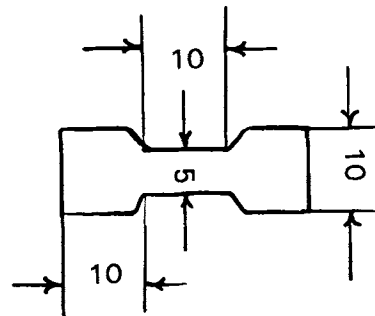$$\sigma_f = \frac{K_m \gamma_2}{\gamma_1 + \gamma_{12}} \qquad (1)$$

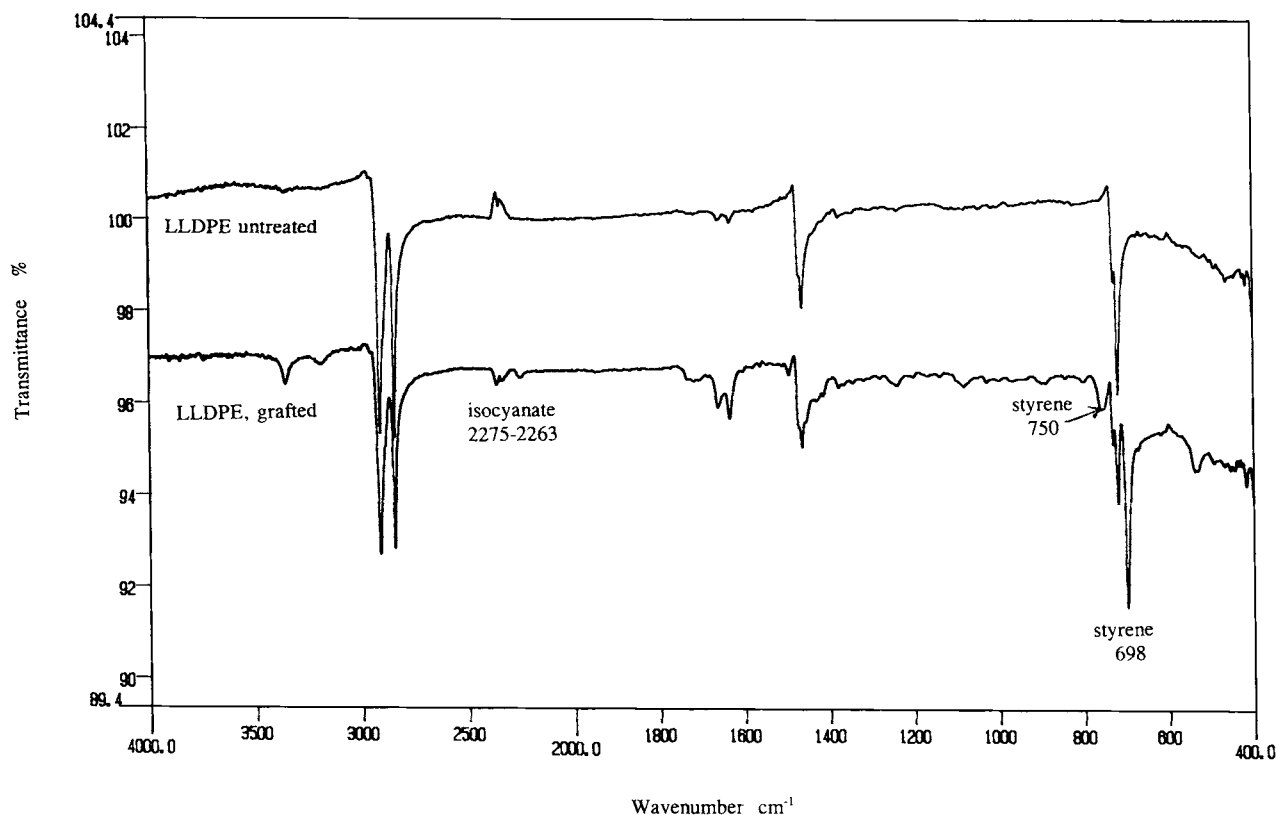**Figure 2**   Dimensions of tensile test samples.

Figure 3   FTIR spectra from comparative analysis of untreated LLDPE and S-MTMI-grafted LLDPE fiber.

According to eq. (1), a plot of σ_f vs. $\gamma_2/(\gamma_1 + \gamma_{12})$ for a series of adhesive bonds should give a straight line provided that the mechanical parameter K_m can be regarded as practically constant. For a given adhesive on a series of different solid surfaces, γ_1 is constant, and since usually $\gamma_1 \gg \gamma_{12}$, one can conclude from eq. (1) that the bond strength varies linearly with γ_2. The ratio between the polar and dispersive components of two adhering surfaces have an influence on the bond; generally, the bond is better the more alike the values of the dispersive and polar components are for the two surfaces.[4]

Surface Treatment of Fibers

The fibers available for reinforcement of composites are treated mainly with surface finishes for two reasons: either for improving the handleability of the fibers in yarn spinning and subsequent fabric and web formation processes or for ensuring good adhesion to the matrix in the fiber-reinforced composites. The surface treatments of fibers can also be expected to affect the flow behavior of the polymer matrix through fibrous structures during the polymer-injection phase of the fabrication processes for composites.

The surface properties of fibers for use as composite reinforcement are modified in order to increase the bond strength in the interface region. Small amounts (0.001–0.01 mol fractions) of appropriate reactive functional groups can greatly increase the bond strength. Examples of functional groups include carboxyl, nitrogen-containing, hydroxyl, methylol, epoxide, isocyanate, and phosphoric acid groups. Epoxide groups promote adhesion to organic or inorganic surfaces containing active hydrogens such as hydroxyl, carboxyl, amino, and amide groups. Thus, epoxy resins are used to prime p-aramid fibers to improve their adhesion to the matrix in composites, e.g., in rubber products like tires or belts.[4] Treatment of the polyethylene fiber surface with monomers like acrylamide, styrene, or cyanate after electron-beam radiation (preirradiation method) offers a potential possibility to increase the chemical reactivity of the fiber surface.[5] The coating of fibers with fluorochemicals, e.g., homopolymers of fluorocarbons with 7–14 C atoms and monomers like chloroprene or butadiene, is used to decrease the surface energy of the fiber surfaces.[6–9]

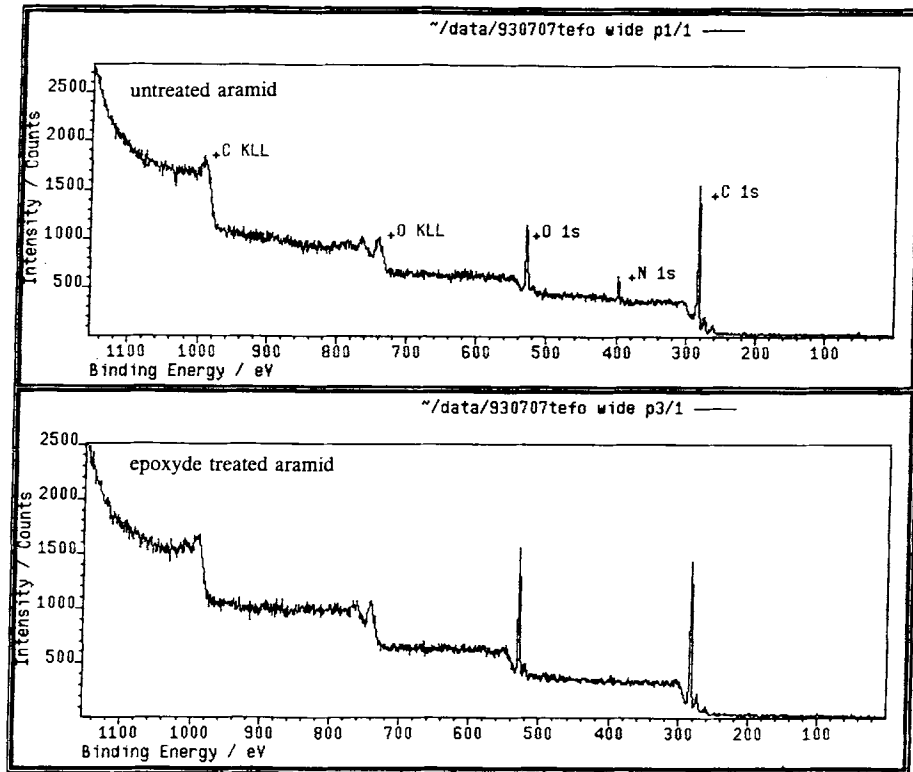The surface properties of polyester fibers can be modified by means of saponification of the PET by

Figure 4 ESCA spectra from comparative analysis of untreated aramid and epoxide-treated aramid fiber. Note the missing peak for nitrogen in epoxy-treated fiber.

means of NaOH to glycol and terephthalate (stripping process) resulting in an increase of the number of carboxyl and hydroxyl groups on the fiber surface.[10,11] The carboxyl and hydroxyl groups have the potential to react with reactive groups, e.g., isocyanate groups in the polymer of the composite matrix. The occurrence of oligomers in the surface region may cause a decrease in the cohesion of the fiber-surface layer after the NaOH treatment.

Mechanical Properties of Composites

Analysis of mechanical properties of fiber-reinforced composite materials as reported in the literature refers predominately to composites containing fibers laid in defined directions or laminae, e.g., unidirectional or woven fibrous structures. The strength properties of composites containing chopped mat that contains randomly distributed fibers are generally lower than of composites containing directional fibers. Since elastomer composites reinforced with randomly oriented long fibers represent a new concept, no information has been found in the literature about their strength properties.[10-16]

Polymer Flow in Fibrous Structures

Surface tension is an important factor influencing the polymer flow. The effect of the pressure gradient on the polymer fluid in pores of fiber structures due to surface tension can be estimated from Laplace's equation by approximating the pore diameter to equal the fiber diameter:

$$\Delta p = \frac{4\gamma_1 \cos \Theta}{d_f} \tag{2}$$

Tadmor and Gogos derived an equation for calculating the fluid flow distance into a capillary under constant pressure from the Poisieuille equation and a mass balance:[13,14]

$$L = \frac{d_f}{4} \left(\frac{\Delta p}{2\mu} \right)^{1/2} t^{1/2} \tag{3}$$

Combining eqs. (2) and (3), one gets

$$L = (d_f \times t \times \gamma_1 \times \cos/4 \times \mu)^{1/2} \tag{4}$$

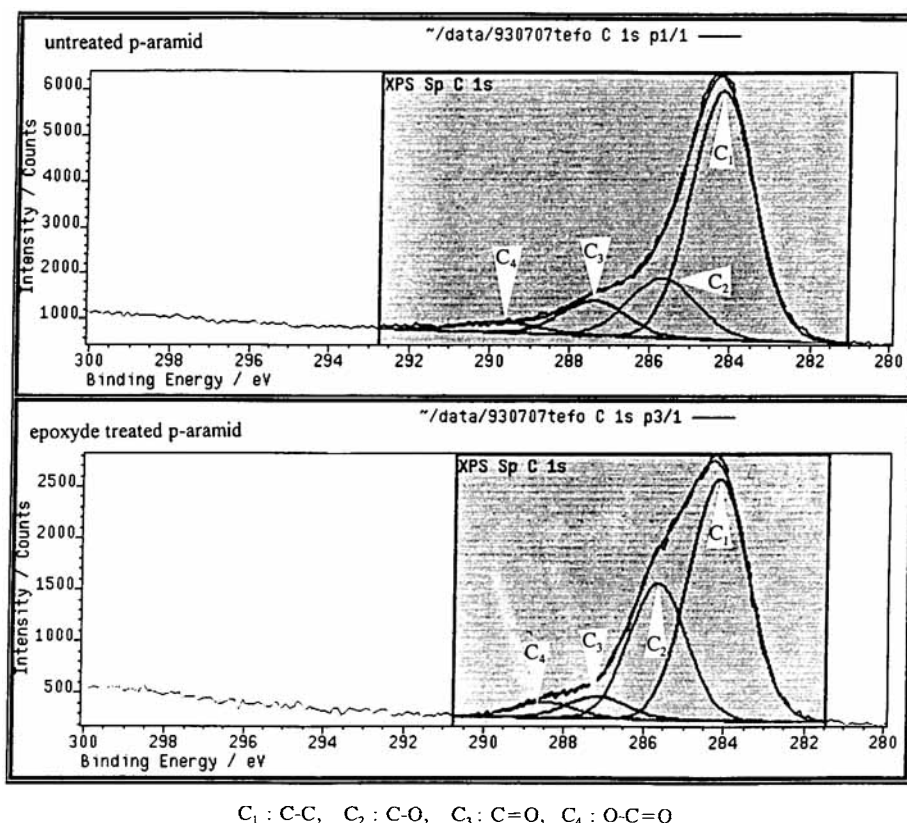C_1 : C-C, C_2 : C-O, C_3 : C=O, C_4 : O-C=O

Figure 5   ESCA analysis of epoxy-treated and untreated aramid fibers. White arrows
refer to peaks corresponding to atomic groups listed below the figure.

which allows the estimation of the distance a polymer
liquid can travel by capillary action in a fiber bundle.[3]

In structural reaction injection molding (SRIM),
it is necessary to select the relevant fiber and fibrous
assembly parameters in order to achieve maximal
flow distances for the matrix resin through the fi-
brous reinforcement structure. The authors have
earlier shown that SRIM process conditions may
require the resin flow to last a long period of time
relative to the pot life of the resin.[1,3]

The aim of the present work was to develop knowl-
edge regarding the influence of fiber-surface charac-
teristics on the flow behavior of elastomer matrix fluid
within the fibrous structures during SRIM molding of
elastomer composites. The influence of parameters
such as the fiber-surface characteristics, fiber dimen-
sions, and fiber volume fraction on the strength of
elastomer composites was also investigated.

EXPERIMENTAL

Test Materials

The test materials consisted of different types of
fibrous structures made from a number of fiber types

and of matrix polymers of two different types. Sur-
face treatments of the fibers were made either to
change the surface energy or to change the chemical
reactivity of the fiber surfaces.

The fibers and matrix used were all of commercial
grade, except for one experimental polyethylene fiber
(4.4 dtex Neste). Polyester, polyethylene, and p-ar-
amid fibers of varying fiber fineness were used. The
fibrous reinforcement structure consisted of need-
lebonded mats made from staple fibers by consec-
utive opening, carding, laying, and needling pro-
cesses. A detailed description of the fabrication and
the properties of the mats used in the experiments
with the polyurethane matrix can be found in some
earlier publications.[1-3]

The matrix used in the SRIM tests was a poly-
urethane elastomer (Baytec from Bayer AG). The
isocyanate part consisted of 1 mol polyol (polyether)
and 2 mol 2,4-TDI. The polyol was of grafted poly-
ether–polyol type [poly(propylene glycol)] with 10%
primary aromatic amine. The polyol also contained
small amounts of catalytic activators. The mixture
showed practically Newtonian behavior up to 4 min
aging time, after which the viscous behavior became
clearly time-dependent. Figure 1 shows the rate of
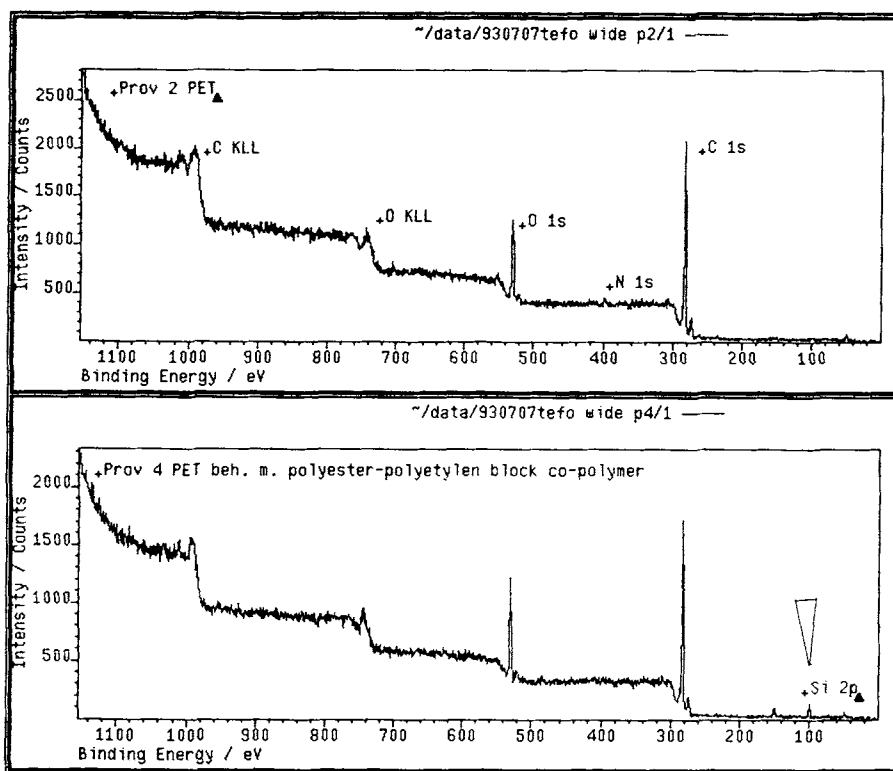change in viscosity of the matrix polymer at different

Figure 6   ESCA spectra from comparative analysis of untreated PET fiber and PET–PG–E-treated PET fiber. Note peak (under pointer) for Si and slight increase in peak for O in PET–PG–E-treated fiber.
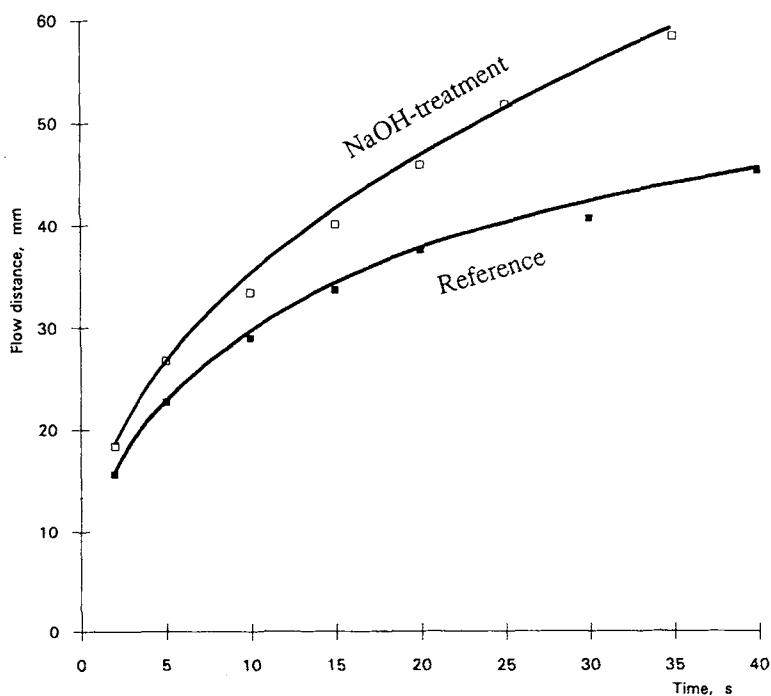

Figure 7   Effect of NaOH treatment of 1.7 dtex PET fiber mat on flow rate of polyurethane elastomer in SRIM at 25% level of compression and 2.6 bar pressure.
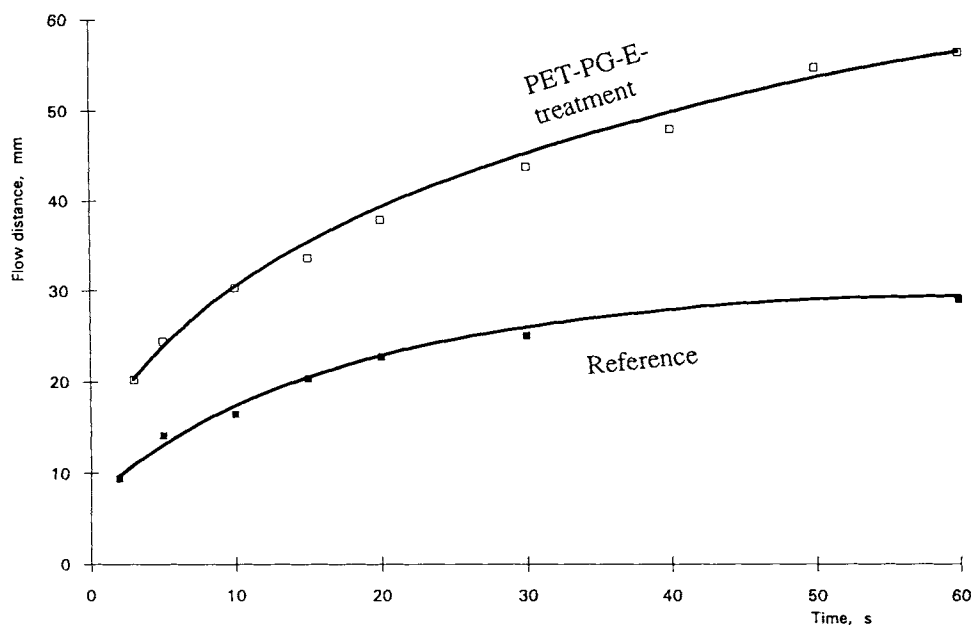
Figure 8   Effect of PET–PG–E treatment of 1.7 dtex PET fiber mat on flow rate of polyurethane elastomer in SRIM at 25% level of compression and 2.6 bar pressure.

initial temperatures of polyol and isocyanate. For the experiments, a natural rubber matrix latex of natural rubber with added vulcanizing and coagulating agents as well as latex of polyurethane dispersion were used. A more detailed analysis of the rheological and chemical properties of the polyurethane matrix polymer and the latex-type matrices was reported earlier by the authors.[2,3]

Surface Treatments on Fibers

The surface energy of the polyurethane matrix is given in Table I from the measurements described below. The surface treatment on the fibers was done either at the stage of the fiber production or subsequent to the fabrication of mats. Different types of treatment used are described below.

Treatment Group I

The first group of treatments was designed to change the surface energy of the fibers. Mats of 1.7 dtex polyester fibers were rinsed in methanol followed by impregnation in an aqueous dispersion of a fluorocarbon containing 5–7 carbon atoms and 45% flour (Quecophob BSN from Thor Chemie). The specimens were then centrifuged for 3 min and subsequently dried at 80°C, leaving an add-on of 0.03–0.06%. Similar mats were rinsed in methanol and then treated with a PET–PG–E copolymer (Permalose TM from ICI), as a water dispersion, at

130°C for 40 min at 2.7 bar followed by rinsing with water in a Werner Mathis Laborjet laboratory dyeing apparatus. Then, the samples were dried at 60°C.

Another treatment consisted of methanol-treated polyester mats being rinsed in methanol and then treated in NaOH solution (45 g/L) at 95°C for 15 min. The specimens were then rinsed in deionized
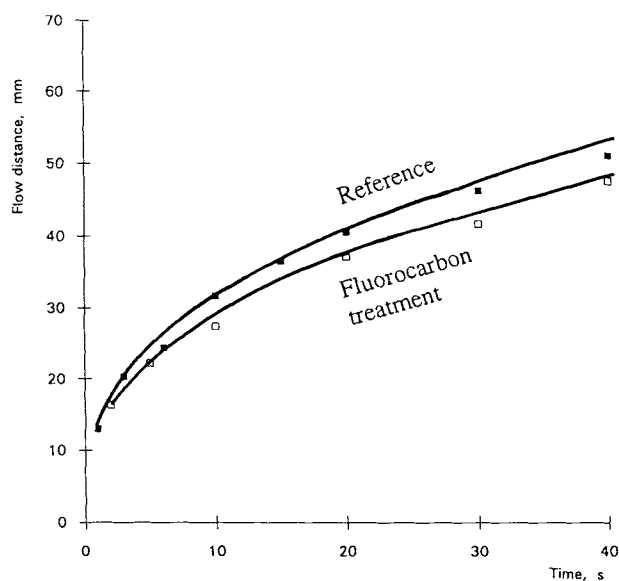

Figure 9   Effect of fluorocarbon treatment of 1.7 dtex PET fiber mat on flow rate of polyurethane elastomer in SRIM at 25% level of compression and 2.6 bar pressure.

Table II   Influence of Surface Energy on Flow Rate in SRIM Fabrication Process

Fiber	Treatment	Surface Energy, Solid (Harmonic-Mean Method) ($\times 10^{-3}$ N/m)			Flow Rate Compared to Index (%)
		Dispersive	Polar	Total	
PET	NaOH	18.9	10.7	29.5	25
PET	Fluorocarbon	22.1	8.2	30.3	−10
PET	PET–PG–E	22.5	20.7	43.2	80

water until the pH reached 7 and then dried at 60°C. The treatment caused a weight loss of 5–7% with only a slight change in the fiber diameter.

Individual fibers of polyester were also surface-treated using the procedures described above for mats. These fibers were used as a substrate for microdroplets in microbond testing of the adhesion strength between a single fiber and the polyurethane matrix.

Another set of mat specimens were subjected to treatments described above except for the addition of fluorocarbon, PET–PG–E, or NaOH. These

specimens were used as reference samples and will later be referred to as reference mats in their respective treatment groups.

Treatment Group II

The objective of the second group of treatments was to produce chemically reactive fiber surfaces. Mats of polyethylene (LLDPE) were electron-beam-radiated in an Electrocurtain electron accelerator under nitrogen atmosphere at 50 kGy on each side of the mat to introduce radicals as preparation for sub-
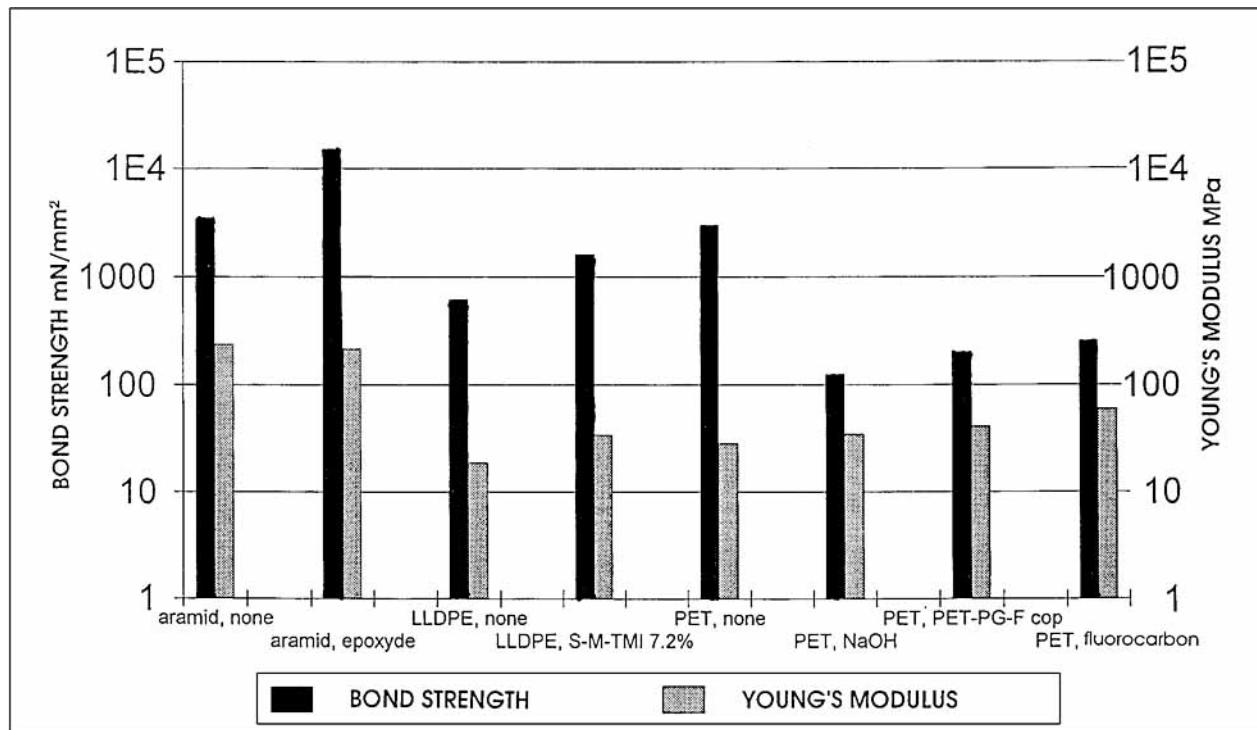

Figure 10   Comparison of Young's modulus and microbond strength for SRIM composites containing aramid, LLDPE, and PET fibers with different surface treatments. Fibers in composite samples: PET 1.7 dtex, modulus 6.2 GPa; LLDPE 4.4 dtex modulus 0.4 GPa; aramid 1.7 dtex, modulus 80 GPa.
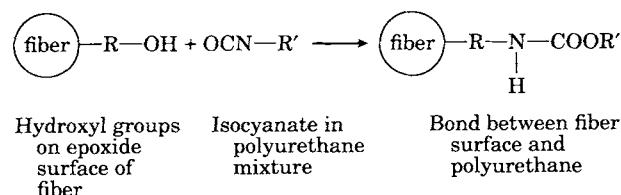
Figure 11   SEM analysis picture of fracture region from tensile test of SRIM composite containing epoxide-treated p-aramid fiber. Original picture 200×.

sequent grafting. The grafting was made by sub-merging the mats into a mixture containing 75% styrene (S) and 25% meta-isopentyl–dimethyl–ben-zoylisocyanate (MTMI) monomers in a bath at 23°C under a nitrogen atmosphere for 0.5 h. Then, the mats were extracted with chloroform at 60°C over-night to remove traces of the monomer. In the graft-ing process, the radicals react with the styrene, the styrene then reacts with the MTMI monomers to form a graft, which then reacts with the polyol com-ponent of the polyurethane elastomer mix:

bond between grafted fiber
and polyol of polyurethane
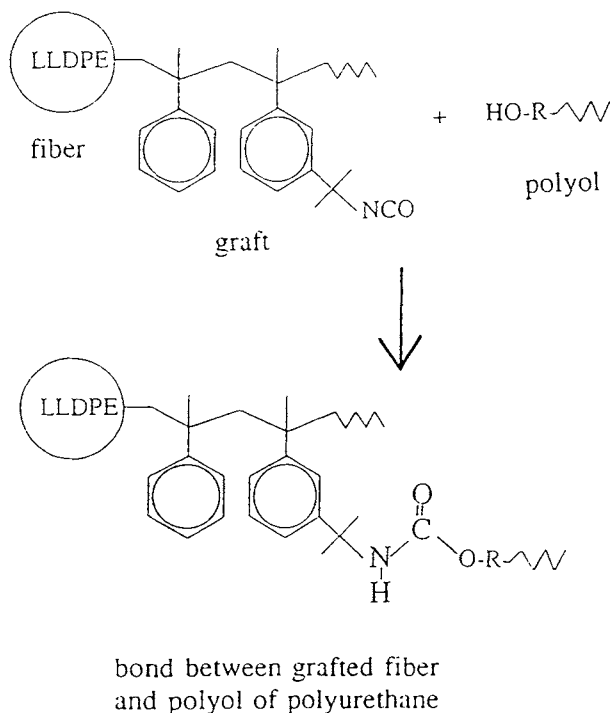
The grafting process, later called S-MTMI grafting, was carried out at the Laboratory of Polymer Tech-nology, Åbo Akademi University.

p-Aramid fibers were coated with cured epoxyde (diglycidyl ether of glycerol) containing piperazine (2.5% dry-on-dry) and a wetting agent (Aerosol OT, 0.5%) and traces of chlorine. The add-on of the coating was 0.5% on the weight of the fiber. The coating was done by means of impregnation and subsequent drying by Akzo fibers. The cured epoxide coating had reactive hydroxyl groups which could react chemically with the isocyanate component of the matrix polymer as shown below:

Hydroxyl groups
on epoxide
surface of
fiber

Isocyanate in
polyurethane
mixture

Bond between fiber
surface and
polyurethane

Testing of Fabrication Process- and Composite Product-related Parameters

The fabrication-related studies consisted of analysis of the flow of polyurethane elastomer fluid in fibrous structures during the SRIM. The contact angles and surface energy of fibers and the polyurethane elas-tomer were also measured. Elastomer flow was in-vestigated according to methods described in earlier publications.[1,3] Comparative elastomer composite samples with a matrix of natural rubber were made using the LC process described earlier by the au-thors.[2]

The contact angle and surface energy of the fibers and matrix were measured using a dynamic micro-balance contact angle device (Cahn DCA-322) which measures the contact angle using the Wilhelmy plate method. The perimeter of the fiber was tested using a microscopic measurement.

The contact angle against two liquids with dif-ferent surface energies, water, and methylene iodide made possible the calculation of the dispersive, polar, and total surface energies of a fiber or film surface by means of the harmonic-mean method used in the Young's equation.[4] The contact angles and surface energy of the polyurethane matrix were approxi-mated by testing a strip of thin polyurethane elas-tomer film of known width and thickness with the microbalance.

The chemical composition of the fiber surfaces was examined by infrared spectroscopy (FTIR) on a Bio-Rad FTS 40 analyzer and/or by electron spec-troscopy for chemical analysis (ESCA) using an Axis HS (Kratos) instrument.
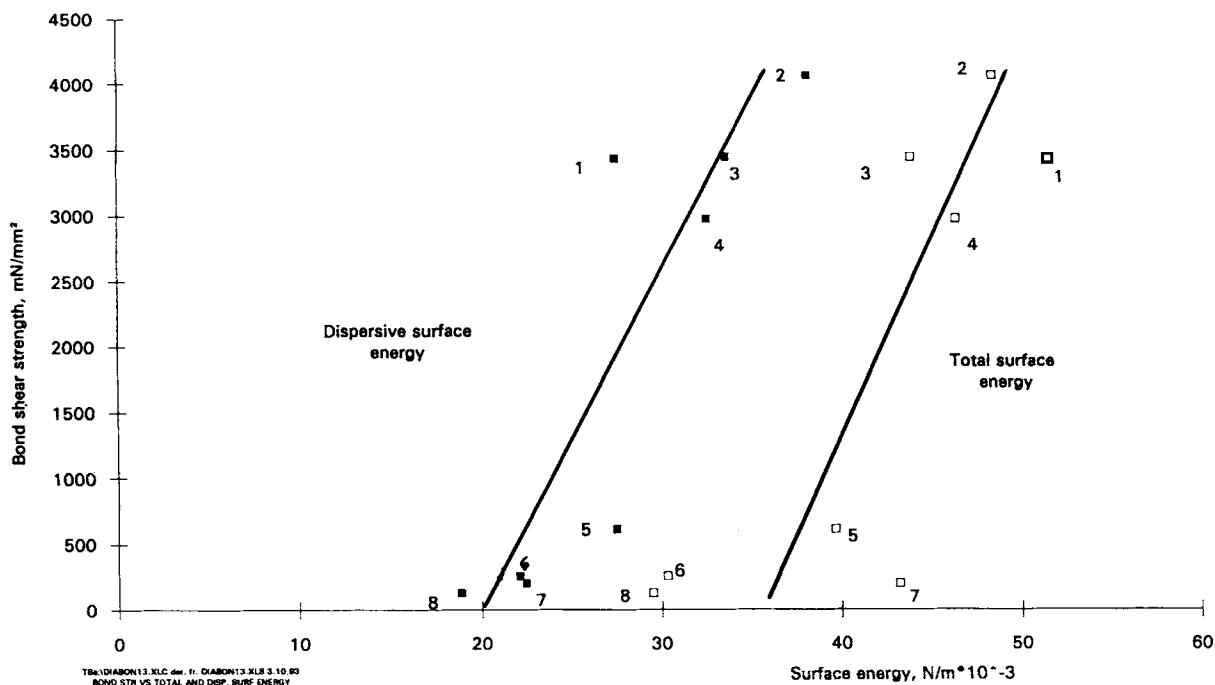
Figure 12 Microbond strength between fiber and polyurethane elastomer vs. total surface energy and dispersive component of surface energy of the fiber surface. (1–5) untreated fibers: (1) aramid; (2) PET, 1.7 dtex; (3) PET, 1.1 dtex; (4) PET, 4.4 dtex; (5) LLDPE, 4.4 dtex; (6–8) treated fibers: (6) PET; 4.4 dtex, fluorocarbon treatment; (7) PET, 4.4 dtex, PET–PG–E treatment; (8) PET, 4.4 dtex, NaOH treatment. Values for 1–3 from Ref. 15.

The testing of composite product-related parameters consisted of microbond strength measurements in order to evaluate the adhesion between the fiber and matrix elastomer and of tensile testing of elastomer composites. Microbond tests were carried out on the surface-treated polyester fibers as well as on the grafted LLDPE fibers using the technique reported in an earlier publication.[15] From the same publication, the test values for epoxide-treated p-aramid fibers and untreated p-aramid fibers were taken for comparison. Microbond tests using polyurethane matrix of different ages on untreated polyester fibers were also carried out.

The mechanical properties of the fabricated composites were tested using an Instron 4502 tensile tester. The rate of deformation was 100 mm/min; the sample size and shape is shown in Figure 2. Composites containing the polyurethane matrix and mats of treated and untreated polyester, p-aramid, and polyethylene fibers were tested. For comparison purposes, the composites reinforced with mats of untreated polyester fibers and having a matrix of natural rubber instead of polyurethane were also tested. SEM analyses were made of some of the surface-treated fibers and of the fiber fracture areas obtained in the extension-to-break experiments.

RESULTS AND DISCUSSION

Effect of Surface Treatment on Fiber-surface Properties

The effects of the surface treatments on the composition of the fiber surface were analyzed by chemical analysis and measurement of the surface energy.

Surface Analysis by Chemical Means

FTIR analysis of the S-MTMI-grafted LLDPE fiber surfaces indicated the presence of isocyanate and styrene as shown in Figure 3, which also shows the transmission spectrum for the untreated LLDPE fiber. In the spectrum of the S-MTMI-grafted fiber, peaks of styrene appear at wavenumbers 698 and 750 cm^{-1} and peaks of isocyanate at 2263 cm^{-1}.

The epoxide-treated and the untreated p-aramid fibers were analyzed using ESCA analysis that showed a lower nitrogen content in the surface of the treated fibers compared to the untreated ones (Fig. 4). This was interpreted to occur because the nitrogen-free epoxide coating blocked the access of the ESCA instrument to the nitrogen atoms of the aramid fiber. Figure 5 shows a comparison of the epoxy-treated and untreated p-aramid fibers using
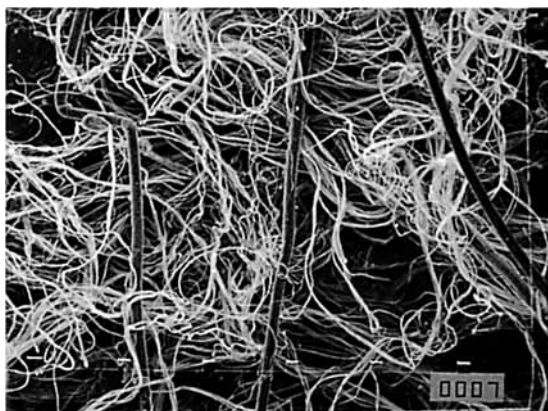
Figure 13   SEM analysis picture of fracture region from tensile test sample of composite containing untreated *p*-aramid fibers. Original picture 200×.

the technique of curve-fitted C1s peaks in ESCA. A significant increase in the C_2 top indicates increase of C — O. The C — O group is interpreted as a further indication of the presence of epoxide in the fiber surface.

Figure 6 shows the result of ESCA analysis of the PET-PG-E-treated and untreated PET fibers. The results showed a slightly lower content of carbon (77.5 vs. 91.5 atom %) and a slightly higher content of oxygen (17.1 vs. 16.5 atom %) in the PET-PG-E-treated sample compared with the untreated

specimen. Since the polyglycol part of the copolymer contains more oxygen and less carbon than does a PET chain of a corresponding number of atoms, the ESCA analysis was interpreted to indicate that the surface contains PET-PG-E. The ESCA analysis of the treated fiber shows the presence of Si, which was not present in the untreated fiber. The occurrence of Si was further confirmed by semiquantitative X-ray-fluorescence analysis of a sample of PET-PG-E that showed a Si content of ca. 0.1% dry-on-dry. This occurrence of Si has been traced to the glass residuals from the glass-ball mill treatment of PET-PG-E during manufacturing.[9]

Surface Energy Measurement on Fibers and Polyurethane Matrix

The results showed that no significant difference occurs between untreated and epoxide-treated *p*-aramid as regards both dispersive and polar components of the surface energy. For polyester fibers, for the treatments with fluorocarbon and NaOH, the analysis indicated lower total surface energy, whereas the PET-PG-E copolymer treatment resulted in only a small change. These results are in agreement with those reported by earlier workers.[16,17] The fluorocarbon treatment gave a larger decrease in the polar component. NaOH treatment caused a larger decrease in the dispersive component. The
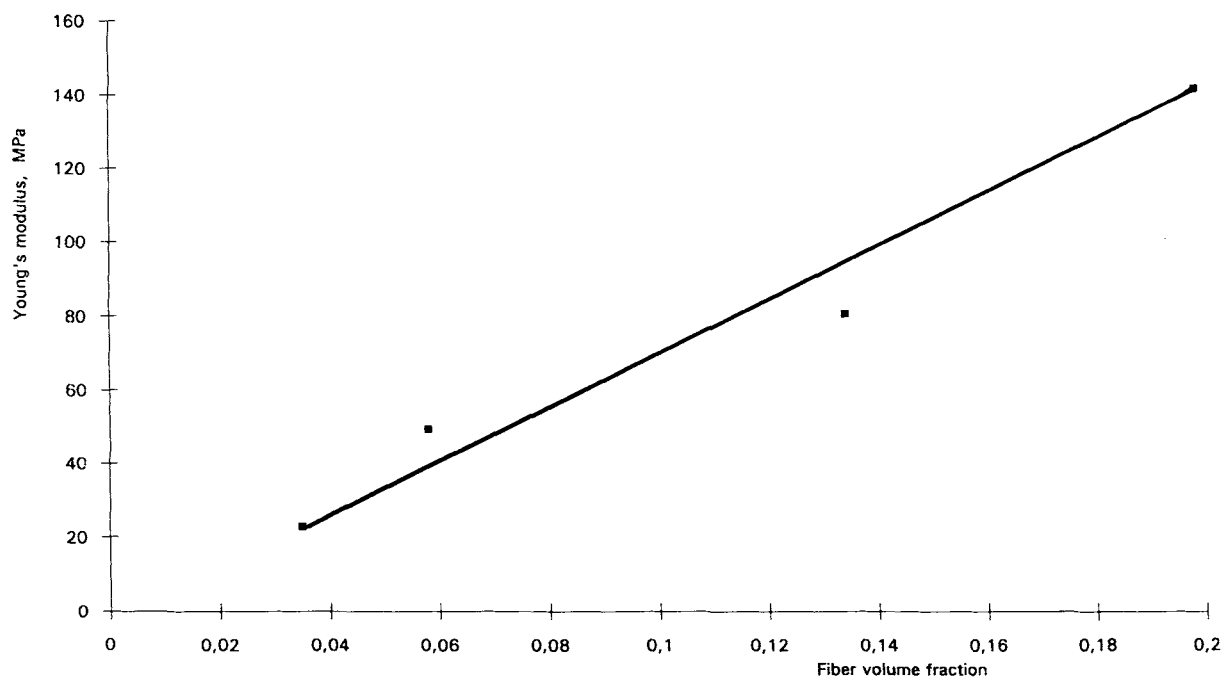

Figure 14   Young's modulus as function of fiber volume fraction; 1.7 dtex PET fibers in polyurethane SRIM composites.
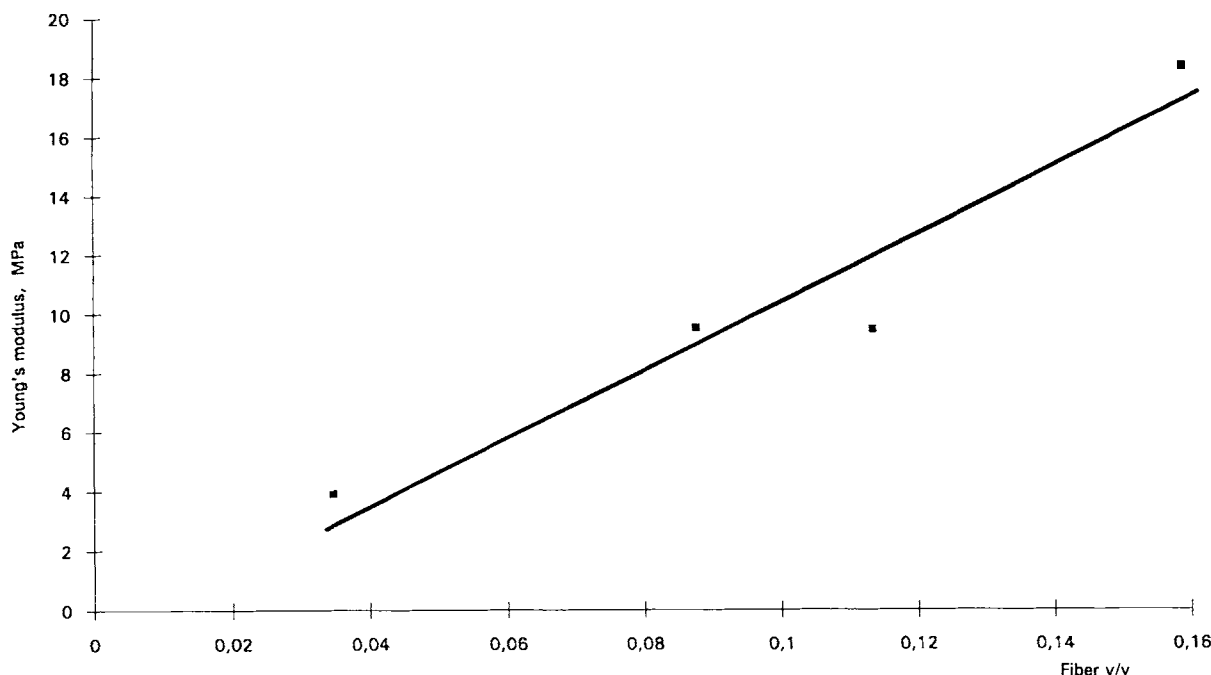
Figure 15   Young's modulus as function of fiber volume fraction; 6.2 dtex PET fibers in natural rubber LC composites.

PET–PG–E copolymer treatment caused an increase in the polar component but a somewhat larger decrease in the dispersive component, thereby causing a slight lowering in the total surface energy. The fluorocarbon treatment also caused the contact angle for water against the fiber to increase, whereas the PET–PG–E copolymer treatment decreased the contact angle for water against the fiber, which is in agreement with the results published elsewhere.[16-20]

The dispersive component obtained in case of a cured film of the polyurethane matrix was much larger than was the polar component. Thus, the surface-energy properties of the matrix elastomer were more or less similar to those of the fluorocarbon-treated fiber. The results of the analysis of surface energy of fibers with different surface treatments are given in Table I.

Investigations of Influence of Surface Properties on Polymer Flow in SRIM Molding

Experiments were made to study the effect of the fiber surface on the flow behavior of the polyurethane matrix elastomer during the SRIM. The flow rates of the polymer in the surface-treated polyester mats were compared with the flow rates obtained for the corresponding reference specimens. It can be seen from Figures 7 and 8 that NaOH-treated mat exhibits an increase of ca. 25%, and PET–PG–E copolymer-treated mat, an increase of ca. 80% in the flow rates compared to the corresponding reference samples, respectively. The fluorocarbon-treated mat shows a 10% decrease in flow rate as compared with the reference sample (Fig. 9). The flow rate was greatest in mats containing fiber with a higher total surface energy as predicted by eq. (1) with the fiber representing the solid surface and the matrix being the adhesive. As can be seen from Table II, the flow rates are also higher in the case of mats of fibers exhibiting greater values for the polar component of the surface energy.

However, the treatment processes were observed to significantly affect the structure of mats which had undergone treatment without fluorocarbon, PET–PG–E, or NaOH. The mats showed various degrees of compaction due to the treatment processes. The treatment for the PET–PG–E copolymer caused a 26% reduction in the thickness and the NaOH treatment caused an 8% reduction. No thickness change was noted due to the fluorocarbon treatment. The treatments involving NaOH and the PET–PG–E copolymer also caused considerable changes in the flow rates, the flow rates being 15 and 55%, respectively, of the corresponding flow rate values for untreated as well as fluorocarbon-treated mats.
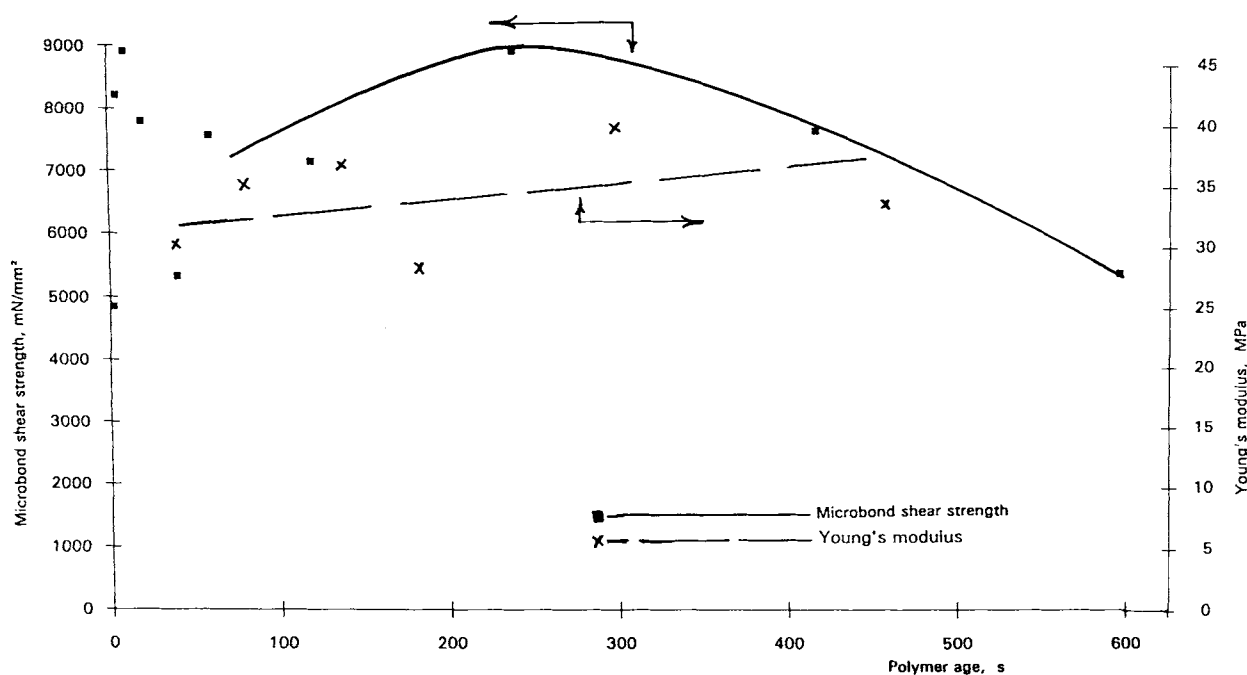
Figure 16 Effect of the polymer age on the microbond strength between fiber and polymer and on the Young's modulus of composites, PU; elastomer composites with 1.1 dtex PET fibers.

The values for the flow rate presented above correspond to a 25% level of compression. At higher compression levels, the differences between treated and reference samples decreased considerably.

Mechanical Properties and Fracture Appearance as Function of Fiber-surface Properties

The effect of surface energies of fibers and the matrix on bond strength and on some mechanical properties of the composites was investigated using an Instron tensile testing equipment. The influence of fiber-surface treatments on the Young's modulus of the composite and bond strength can be seen in Figure 10. The results show a significant difference in bond strength between untreated and treated LLDPE and p-aramid fibers. The Young's modulus of the composites, however, does not seem to be influenced by the reactive surface treatments on these fiber types. In the case of p-aramid fibers, this can be due to fibrillation as seen in Figure 11, and in the case of the grafted polyethylene fibers, it may be due to a weak interface layer, although it could not be seen in the SEM pictures. Fibrillation will not affect the strength results obtained in microbond tests, whereas it would significantly affect the Young's modulus of the composite.

Results from Analysis of Bond Strength and Young's Modulus

It can be seen from Table I that the bond-strength values of the fluorocarbon-treated PET fibers having similar values for the two components of the surface energy as those of the matrix was greater than for PET fibers treated with NaOH or PET–PG–E copolymer. The NaOH and PET–PG–E treatments did not give as high a degree of similarity in surface energy with the matrix as did the fluorocarbon treatment. As can be seen from Figure 12 and as predicted by eq. (1), the microbond strength values obtained for the surface-treated PET fibers (fluorocarbon, NaOH, and PET–PG–E) correlated well with the total surface energy (correlation factor .82) and also with the dispersive component (correlation factor .89).

The good correlation obtained between bond strength and the dispersive component of surface energy indicates that the dispersive component of the surface energy for the polyurethane matrix plays a significant part. No correlation was found between the Young's modulus for composites and the surface energy of mats treated with fluorocarbon, PET–PG–E, and NaOH. The low bond-strength values obtained in case of NaOH-treated PET fibers despite the occurrence of carboxyl and hydroxyl groups on

the surface may be due to the molecular scission occurring at the fiber surfaces as a result of the alkali treatment.

Results from SEM Analysis of Fractures from Tensile Tests

The SEM analysis of the fracture regions in composites made of untreated PET fiber showed some unevenness in the surface of the imprints of fibers in the matrix. Fewer traces of the polymer were seen on the surfaces of fiber ends in the fracture regions of composites containing polyester fibers treated with fluorocarbon, PET–PG–E, and NaOH. None of the effects described above was found in composites containing untreated fibers. Figures 11 and 13 show matrix polymer traces adhering to fiber ends of epoxide-treated p-aramid fibers. In addition to giving higher bond strength and modulus, the composite samples made from mats containing surface-modified fibers showed significantly more traces of matrix left on fiber ends after strength determination of the composites based on these fiber types. Both the epoxide-treated and the untreated p-aramid fibers showed severe fibrillation (Figs. 10 and 13). Fiber fractures were seen in the fracture areas of all specimens from the tensile tests.

Influence of Fiber Volume Fraction, Polymer Age, and Matrix Type on Young's Modulus of Composites and Bond Strength

The effect of fiber volume fraction, fiber modulus, and polymer age on the mechanical properties of composites was investigated by means of tensile testing and bond-strength testing. The deformation of the matrix as well as the destruction of fiber due to defibrillation during failure of the composite material was investigated by means of SEM analysis. The deformation of the composites was also studied on the test specimens from the tensile tests by length measurements 3 months after the test. No attempt was made in this work to study the relationship between the flow rate in the filling process and the Young's modulus of the composite.

Fiber Volume Fraction

The effect of the fiber volume fraction on the Young's modulus of composites was tested on samples with varying volume fractions. SRIM composites based on polyester fibers and the matrix of polyurethane and LC composites with a natural rubber matrix were tested. It can be seen from Figures 14

and 15 that the Young's modulus of polyurethane composites correlates well with the fiber volume fraction in these specimens. The interaction between the Young's modulus of the fiber on the Young's modulus of the composite was investigated in the case of some specimens. Composites reinforced with untreated p-aramid fiber which have a modulus of 80 GPa exhibited several times higher values of the Young's modulus than did composites containing corresponding mats of untreated polyester which have a modulus of 6 GPa.

Polymer Age

The influence of the age of the polymer on the Young's modulus of the composite has been investigated using elastomer of different ages (30–500 s). The polymer age is defined as the time interval between the mixing of the components and the SRIM process. As can be seen from Figure 16, the Young's modulus was practically uninfluenced by the polymer age. This figure also shows that the bond strength after reaching a maximum at ca. 250 s drops significantly thereafter. This indicates that the age of the matrix at the time of contact with the fiber plays a part in the bond strength.

CONCLUSIONS

The effects of the surface treatment of fibers, fiber volume fraction, and polymer age on the matrix flow and mechanical properties in elastomer composites were investigated. The results show that those surface treatments which produced a change in the surface energy of fibers have a significant influence on the matrix flow in the SRIM fabrication of composites.

The treatments which produced chemically reactive fiber surfaces resulted in improvement in bond strength between fibers and the polyurethane matrix. No increase was noticed, however, in the Young's modulus of SRIM-molded composites containing untreated and treated fibers. Good correlation was obtained between the bond strength, on the one hand, and the total and dispersive components of surface energy, on the other. The treatments causing surface-energy changes on fibers caused a decrease in bond strength and the Young's modulus compared with the corresponding untreated fiber. A good correlation was obtained between bond strength and the total surface energy and with the dispersive component of the surface energy.

The age of the polyurethane matrix has a significant influence on the bond strength between fibers and the polyurethane matrix. SEM analysis shows signs of poor bonding between the polyurethane elastomer and fibers due to the lack of a chemical bond, insufficient strength of the physical bond, or weak interface layer. The rather large difference in modulus between the fibers and matrix may also play a part in the debonding mechanism. Considerable deformation of the matrix occurred in the fraction surfaces of the composites. Fiber fractures were seen in all composite samples from tensile testing.

The Young's modulus of the composite is influenced by the fiber volume fraction for both SRIM and LC composites. The modulus of the single fibers had influence on the Young's modulus of the composite. No correlation was found between bond strength and the Young's modulus of composites containing fiber reinforcement of randomly placed fibers in a three-dimensional fibrous structure.

NOMENCLATURE

d_f fiber diameter
K_m mechanical parameter
L distance of liquid or polymer travel;
         wetted length
t time
v velocity
γ_1 surface energy of adhesive (matrix)
γ_2 surface energy of solid (fiber)
γ_{12} surface energy between adhesive and solid

Δp pressure difference; driving pressure
σ_f fracture strength
Θ contact angle
μ viscosity

REFERENCES

1. M. Epstein and R. L. Shishoo, *J. Appl. Polym. Sci.,* **45**, 1693 (1992).
2. M. Epstein and R. L. Shishoo, *J. Appl. Polym. Sci.,* **44**, 263 (1992).
3. M. Epstein and R. L. Shishoo, *J. Appl. Polym. Sci.,* to appear.
4. S. Wu, *Polymer Interface and Adhesion,* Marcel Dekker, New York, 1982.
5. K. Ekman, L. Ekholm, and J. H. Näsman, *J. Appl. Polym. Sci.,* to appear.
6. R. Kleber, *Textil. Int.,* **August,** 449 (1972).
7. P. Otto, *Melliand Textil.* **5,** 378 (1991).
8. G. Heidemann, K. Schliefer, C. M. Estrada-Askar, H. K. Rouette, and L. Zhang, *Chem. Textilindust.,* **39/91** (1989).
9. S. H. Zeronian and M. J. Collins, *Textile Prog.,* **20**(2).
10. L. C. Hopper and G. L. Sauer, *Engineered Materials Handbook,* Vol. 1, ASM Int., 1987, p. 290.
11. R. E. Bullock, *J. Compos. Mater.,* **8,** 200–206 (1974).
12. C. Zweben, W. S. Smith, and M. W. Wardle, in *Composite Materials: Testing and Design—Fifth Conference,* ASTM STP 674, 1978, p. 228.
13. J. M. Gere and S. P. Timosenko, *J. Compos. Mater.,* **8**, 253 (1974).
14. Z. Hashin, *J. Mech. Phys. Solids,* **13**, 119 (1965).
15. I. Y. Chang and J. K. Lees, *J. Thermoplast. Compos. Mater.,* **1**, 277 (1988).
16. C. C. Chamis, *J. Comp. Technol. Res.,* **11**(1), 3–14 (1989).
17. Z. Tadmor and C. G. Gogos, *Principles of Polymer Processing,* Wiley-Interscience, New York, 1979.
18. C. W. Macosko, *RIM Fundamentals of Reaction Injection Molding,* Hanser, Munich, 1989.
19. M. Epstein and R. L. Shishoo, *J. Appl. Polym. Sci.,* **50**(5), 863–874
20. R. Gordon, ICI, Bolton England, private communication.